Z-Selective Olefin Metathesis Using Chelating Ruthenium Alkylidene Catalysts

Thesis by
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ABSTRACT

Publications about olefin metathesis will generally discuss how the discovery and development of well-defined catalysts to carry out this unique transformation have revolutionized many fields, from natural product and materials chemistry, to green chemistry and biology. However, until recently, an entire manifestation of this methodology had been inaccessible. Except for a few select examples, metathesis catalysts favor the thermodynamic *trans*- or *E*-olefin products in cross metathesis (CM), macrocyclic ring closing metathesis (mRCM), ring opening metathesis polymerization (ROMP), and many other types of reactions. Judicious choice of substrates had allowed for the direct synthesis of *cis*- or *Z*-olefins or species that could be converted upon further reaction, however the catalyst controlled synthesis of Z-olefins was not possible until very recently.

Research into the structure and stability of metallacyclobutane intermediates has led to the proposal of models to impart *Z*-selectivity in metathesis reactions. Having the ability to influence the orientation of metallacyclobutane substituents to cause productive formation of *Z*-double bonds using steric and electronic effects was highly desired. The first successful realization of this concept was by Schrock and Hoveyda et al. who synthesized monoaryloxide pyrolidine (MAP) complexes of tungsten and molybdenum that promoted *Z*-selective CM. The *Z*-selectivity of these catalysts was attributed to the difference in the size of the two axial ligands. This size difference influences the orientation of the substituents on the forming/incipient metallacyclobutane intermediate to a cis-geometry and leads to productive formation of *Z*-olefins. These catalysts have shown great utility in the synthesis of complicated natural product precursors and stereoregular polymers. More recently, ruthenium catalysts capable of promoting *Z*-selective metathesis have been reported by our group and others. This thesis will discuss the development of ruthenium-based NHC chelated *Z*-selective catalysts, studies probing their unique metathesis mechanism, and synthetic applications that have been investigated thus far.

Chapter 1 will focus on studies into the stability of NHC chelated complexes and the synthesis of new and improved stable chelating architectures. Chapter 2 will discuss applications of the highly active and *Z*-selective developed in Chapter 1, including the formation of lepidopteran female sex pheromones using olefin cross metathesis and highly *Z*- and highly *E*-macrocycles using macrocyclic ring closing metathesis and *Z*-selective ethenolysis. Chapter 3 will explore studies into the unique mechanism of olefin metathesis reactions catalyzed by these NHC chelated, highly *Z*-selective catalysts, explaining observed trends by investigating the stability of relevant, substituted metallacyclobutane intermediates.

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DESIGN AND SYNTHESIS OF NHC-CHELATED RUTHENIUM ALKYLIDENE COMPLEXES

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Keitz, B. K.; Endo, K.; Patel, P. R.; Herbert, M. B.; Grubbs, R. H. *J. Am. Chem. Soc*. **2012**, *134*, 693.

Herbert, M. B.; Lan, Y.; Keitz, B. K.; Liu, P.; Endo, K.; Day, M. W.; Houk, K. N.; Grubbs, R. H. *J. Am. Chem. Soc*. **2012**, *134*, 7861.

Rosebrugh, L. E.; Herbert, M. B.; Marx, V. M.; Keitz, B. K.; Grubbs, R. H. *J. Am. Chem. Soc*. **2013**, *135*, 1276.

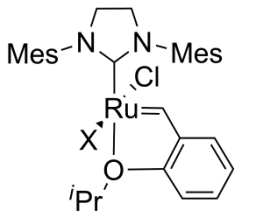
ABSTRACT:

After the serendipitous discovery that NHC-substituted ruthenium alkylidene catalysts could form *Z*-selective, NHC-chelated architectures upon treatment with silver (I) carboxylates, the development of more active and *Z*-selective catalysts was desired. Studies into the decomposition of chelated complexes and analogous dipivalate-substituted precursors were performed. These led to the elucidation of important information about the stability of chelated catalysts and ways to prevent the formation of undesired side-products. A milder method for the salt metathesis and C-H activation was then devised, where sodium carboxylates were used in place of silver (I) carboxylates. This strategy circumvented many of the elucidated decomposition modes and has led to the isolation of new and improved olefin metathesis catalysts. More recent efforts were aimed at replacing the standard *N*-1-adamantyl chelate with other *N*-chelating groups to investigate the scope of complexes that can form a stable chelate and concurrently test these new alkylidene complexes as olefin metathesis catalysts.

INTRODUCTION:

Early efforts to design ruthenium catalysts that could catalytically produce *Z*-olefins involved synthesizing *N*-heterocyclic carbene (NHC) substituted complexes where a single chloride ligand was replaced by a large anionic ligand (Figure 1). This strategy led to the synthesis of many new catalysts that contained sterically hindered sulfate or phosphate ligands, and exhibited slightly decreased *E*/*Z* ratios compared to the dichloride starting catalysts.[1] Preliminary DFT calculations predicted that an analogous catalyst with a pivalate ligand replacing one of the chlorides of an NHC-substituted ruthenium alkylidene catalyst (**1.1**) would be *Z*-selective. In attempting to prepare this catalyst, we serendipitously were able to form NHC-chelated architectures and thus the first *Z*-selective ruthenium metathesis catalyst was formed.

Later, it was found that replacing a chloride with a sterically hindered 2,4,6-triphenyl thiophenol resulted in the formation of a *Z*-selective catalyst based on the original design.[2]

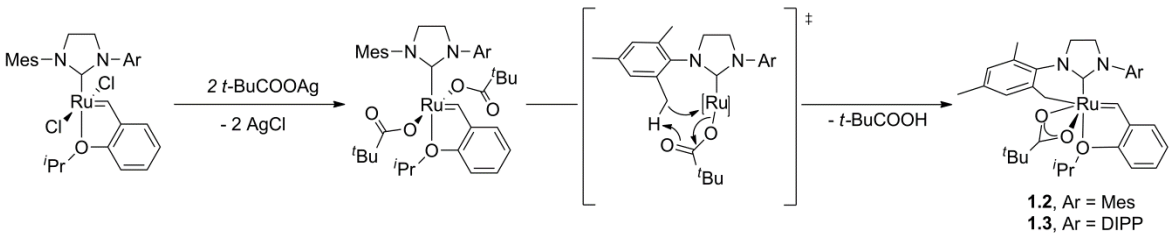


$X = RSO_3^-, RP(O)O^-$

1.1, $X = Cl^-$

Figure 1: NHC-substituted ruthenium alkylidene catalysts. Mes = 2,4,6-trimethylphenyl.

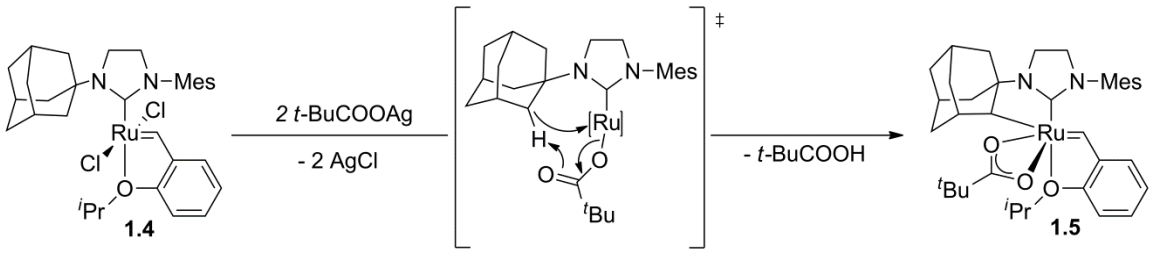
When catalyst **1.1** was exposed to an excess of silver (I) pivalate, instead of a single substitution of a chloride for a pivalate, an unexpected and novel catalyst architecture was formed.[3] This product was purified and subsequently characterized by NMR spectroscopy and X-ray crystallography to reveal a complex that contained a ruthenium-carbon bond derived from C–H activation of the *N*-mesityl substituent on the NHC ligand and thus contained a six-membered chelating architecture (Scheme 1). Instead of observing mono-substitution, two pivalate ligands replaced the two chlorides and the resulting complex underwent a carboxylate-driven C–H bond insertion, presumably through a six-membered transition state as shown. The fact that this complex, bearing a chelating ruthenium-carbon bond and an intact alkylidene, could be isolated was a surprise at first because C–H activation of NHC *N*-substituents generally resulted in the formation of metathesis inactive decomposition products. It was thus surprising that complex **1.2** was metathesis active and, on top of that, showed improved *Z*-selectivity (~40%) in the standard cross metathesis reaction of allylbenzene and *cis*-diacetoxybutene, compared to non-chelated catalysts like **1** that generated ~90% of the *E*-isomer.



Scheme 1: Mechanism of carboxylate-assisted C–H activation to form catalysts **1.2** and **1.3**.

Initial optimization of this catalyst involved replacing the non-chelating *N*-mesityl group with a bulkier group. Substitution with an *N*-2,6-diisopropylphenyl (*N*-DIPP) group led to chelated catalyst **1.3** that exhibited a *Z*-content of just over 50% in the standard CM reaction.[4] It was thus proposed that increasing the steric bulk of the non-chelating *N*-substituent of catalyst **1.2** would further increase the *Z*-selectivity, and thus a dichloride catalyst substituted with an *N*-adamantyl group (**1.4**) was prepared and exposed to excess *t*-BuCOOAg.[3] After C–H activation, a chelated catalyst was formed that exhibited the highest *Z*-selectivity observed to date for a ruthenium-catalyst (~90% in the standard CM reaction). It was originally thought that this complex contained a six-membered chelating architecture and resembled **1.2** and **1.3**, and that the improved *Z*-selectivity was due to the bulkier nonchelated *N*-substituent. However, this complex exhibited properties that set it apart from these species. Instead of the characteristic dark green color observed for complexes **1.2** and **1.3**, this new catalyst was purple in color. Additionally, in the ^{1}H NMR, the proton that was expected to be α to the chelating benzylic carbon was not present and the benzylidene proton resonance was shifted up field by ~1 ppm. Upon X-ray crystal analysis, it was revealed that this catalyst (**1.5**) was actually derived from C–H activation of the *N*-adamantyl group instead of the *N*-mesityl group, and a five-membered chelated architecture had been formed (Scheme 2). In the crystal structure of the unactivated complex **1.4**, the C–H bond of the adamantyl group that is activated sits quite close (~2.8 Å) to the ruthenium center and it thus made sense that the *N*-adamantyl group would be preferentially activated. While catalyst **1.5** exhibited high *Z*-selectivity for a large number of substrates, in some cases *Z*-selectivity was

significantly lower and the conversions ranged from moderate to poor. Thus, efforts were aimed at synthesizing more active and selective catalysts.



Scheme 2: Mechanism of carboxylate-assisted C–H activation to form catalyst **1.5**.

Anionic Ligand Investigations

With *Z*-selective catalyst **1.5** in hand, a number of alterations to improve the activity and selectivity were envisioned. It was discovered that the fastest way to systematically modify these new catalysts was to replace the anionic ligand, and thus this was initially investigated (Figure 2).[5] Iodide-substituted complex **1.6** could be synthesized directly by treating complex **1.5** with NaI. This species proved to be a useful starting material, as **1.6** could be reacted with various silver (I) and potassium salts to generate a variety of complexes with varying anionic ligands. These salt metathesis reactions could be monitored by ^{1}H NMR spectroscopy. If a stable chelated species substituted with a new anionic ligand was formed, a peak would appear and persist at ~15-16.5 ppm over time. In contrast, if the newly formed species was unstable, rapid decomposition to a ruthenium-hydride would occur and the corresponding signal would be observed in the hydride region. This allowed for facile evaluation of a large number of new ligands and isolation of new and improved chelated catalysts.

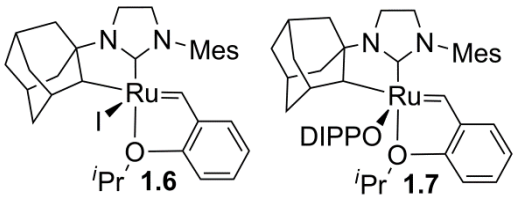


Figure 2: NHC-chelated ruthenium complexes bearing monodentate X-type ligands.

All new isolable chelated catalysts were evaluated in two ways: by investigating their activity and selectivity in selected homodimerization reactions, and by investigating their initiation rates by monitoring their reaction with *n*-butyl vinyl ether over time. It quickly became apparent that the catalyst's activity, in general, was not well correlated with the measured initiation rates. There was, however, a clear correlation for catalysts containing monodentate X-type ligands like iodide (**1.6**) and 2,6-diisopropylphenoxide (**1.7**) (Figure 2). These complexes exhibited very slow initiation and, additionally, showed poor metathesis reactivity, preferentially isomerizing olefin substrates.

In order to investigate the steric effects of the carboxylate ligand, catalysts containing a less bulky acetate (**1.8**) and a more bulky 2,2-dicyclohexylcarboxylate (**1.9**) were synthesized (Figure 3). The initiation rates were found to increase with increased steric bulk of the ligand, however this did not correlate with the metathesis activity of these catalysts. Similarly, when comparing catalyst **1.5** to one substituted with a more electron donating carboxylate ligand (**1.10**), the trend in initiation did not match the trend in metathesis reactivity (Figure 3). Since initiation rates did not correlate with metathesis reactivity, evaluation in a variety of metathesis reactions was envisioned as a way to relate structure and activity.

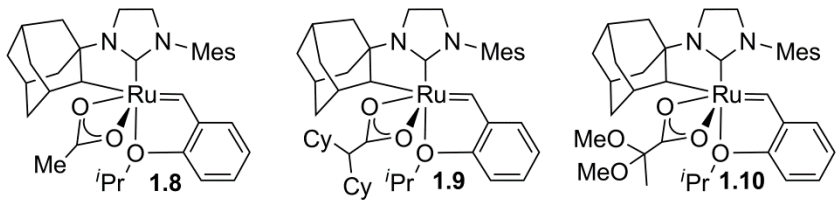


Figure 3: NHC chelated ruthenium complexes bearing carboxylate X-type ligands. Cy = cyclohexyl.

After many iterations of these stable five-membered chelated complexes were successfully synthesized and tested in metathesis reactions, one stood out above the rest. Catalyst **1.11**, substituted with a nitrate ligand, exhibited significantly higher activity and *Z*-selectivity compared to the pivalate substituted catalyst **1.5** (Figure 4). While **1.5** was able to catalyze homodimerization reactions with near 700 turnovers and ~90% Z-selectivity, **1.11** was able to catalyze the same transformation with near 1,000 turnovers and ~95% *Z*-selectivity.

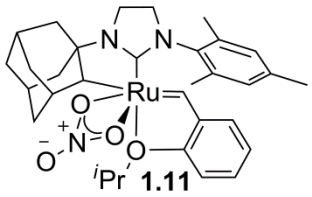


Figure 4: Highly active and *Z*-selective NHC chelated ruthenium complex bearing a nitrate X-type ligand.

N-Aryl Investigations

After the discovery that substitution with a nitrate ligand caused a large increase in activity and selectivity, related catalysts with various *N*-aryl groups were synthesized (Figure 5). It was quickly discovered that changing the *para*-substituent of the *N*-aryl group did not cause a significant change in activity or selectivity, as catalysts **1.12** and **1.13** bearing *para*- methoxy and chloro groups, respectively, showed similar metathesis reactivity and selectivity. In addition, the *ortho*-substituents were varied by replacing the *N*-mesityl with an *N*-2,6-diethyl-4-methylphenyl group (**1.14**), which again showed no significant difference in reactivity compared to catalyst **1.11**.

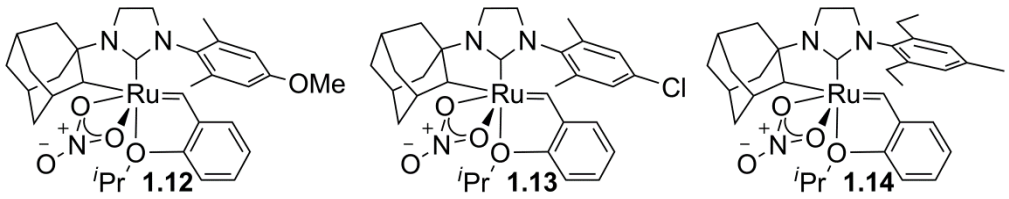


Figure 5: NHC-chelated ruthenium complexes bearing different *N*-aryl groups.

The synthesis of a catalyst containing an *N*-2,6-diisopropylphenyl group was attempted using *t*-BuCOOAg induced salt metathesis and C–H activation, however the catalyst decomposed under the reaction conditions and thus could not be isolated (*vide infra*). Because of the increase in selectivity observed for six-membered chelated catalyst **1.2** versus **1.3**, the isolation of an *N*-adamantyl chelated catalyst containing this bulky *N*-aryl group was highly desired.

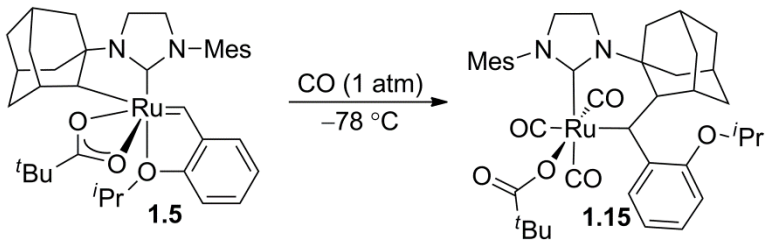
DECOMPOSITION STUDIES:

For the formation of **1.5**, the initial C–H activation event has been proposed to proceed via a six-membered transition state between an alkyl carbon-hydrogen bond on the *N*-adamantyl substituent of the NHC, and a ruthenium-bound carboxylate ligand (Scheme 2).[3] Carboxylate-driven C–H bond activations of this type have been studied for a variety of late transition metal complexes.[6] With this mode of activation, a carbon-metal bond is formed with concurrent generation of the corresponding carboxylic acid. In contrast, previous generations of ruthenium metathesis catalysts have been proposed to decompose upon C–H activation by oxidative addition. This oxidative addition process produces a ruthenium hydride that readily inserts into the alkylidene and diminishes catalytic activity.[7] The unique nature of the carboxylate-driven mechanism allows for isolation of metathesis-active C–H activated complexes without the accompanying formation of a ruthenium hydride.

A thorough understanding of decomposition pathways is important for designing improved catalysts.[7] Research investigating the decomposition of metathesis catalysts has led to the rational design of more stable and active species with ligands chosen to reduce the prevalence of undesired side reactions. For example, backbone substitution was introduced into the NHC ligands of ruthenium catalysts in order to restrict *N*-aryl rotation that leads to the aforementioned oxidative addition decomposition modes.[8] Known decomposition products of metathesis catalysts cause olefin migration of alkene substrates, as well as other side reactions;[9] such migration has been observed in our studies on the *Z*-selective homocoupling of terminal olefins.[5] Computational studies have provided important insights into several decomposition mechanisms involving previous generations of ruthenium metathesis catalysts, including alkylidene insertion into the *ortho* C–H bond of an *N*-aryl substituent,[7f,h] β-hydride elimination from a ruthenacyclobutane intermediate,[7i] and decomposition induced by coordination of CO.[7g] We thus sought to design more selective and stable analogs of catalyst **1.5** by investigating the decomposition of **1.5** and its analogs. Herein, we report on several unique decomposition structures and their mechanisms of formation. To support our mechanisms, density functional theory (DFT) calculations were performed to investigate the proposed decomposition pathways of the C–H activated catalyst **1.5**.

Complex **1.5** was exposed to an excess of CO gas at –78 °C in an effort to promote a (1,1)-insertion of a bound CO ligand into the ruthenium-carbon bond of the chelated NHC to yield a novel chelated catalyst architecture with an intact alkylidene. However, decomposition of the alkylidene moiety was observed and crystallographic analysis revealed formation of **1.15** (Figure 6), an alkyl ruthenium complex saturated with CO ligands and showing covalent attachment of the *N*-adamantyl substituent to the former alkylidene carbon (Scheme 3). Ligand substitution by the π-acidic CO ligands decreased the ability of the metal center to stabilize the alkylidene carbon by back bonding. This destabilization was presumably relieved by insertion of the alkylidene into the ruthenium-carbon bond to form complex **1.15**.[10] It was subsequently proposed that this alkylidene insertion phenomenon could be common for C–H activated catalysts in the absence of

CO, and that ruthenium-alkyl complexes analogous to **1.15** could undergo hydride elimination reactions when not saturated with CO ligands, leading to complexes incapable of productive metathesis.



Scheme 3: Decomposition product **1.15** derived from exposure of **1.5** to excess CO.

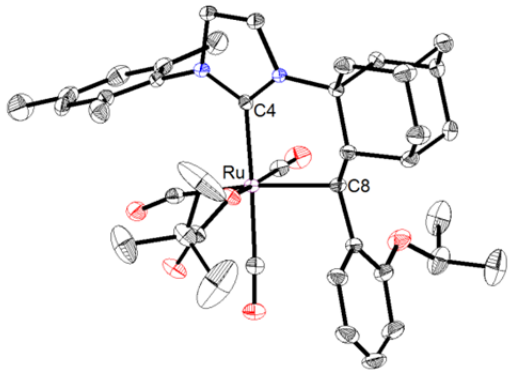
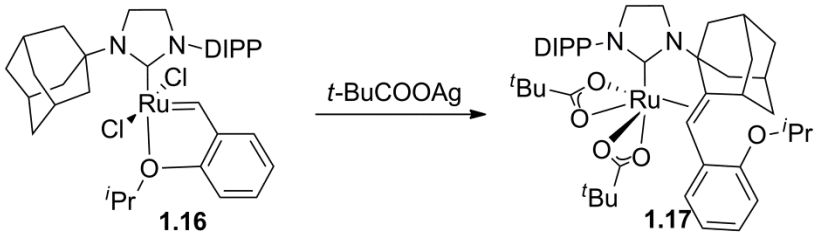


Figure 6: X-ray crystal structure of **1.15**. Displacement ellipsoids are drawn at 50% probability. For clarity, hydrogen atoms have been omitted. Selected bond lengths (Å) for **1.15**: C4-Ru 2.107, C8-Ru 2.195.

Indeed, we were able to isolate a unique decomposition product resulting from alkylidene insertion (as with **1.15**) and subsequent β-hydride elimination when C–H activation was attempted with catalyst **1.16** (Scheme 4).[11] Treating complex **1.16** with silver pivalate (*t*-BuCOOAg) resulted in the expected ligand exchange of chlorides for pivalates, and concomitant generation of silver (I) chloride. Monitoring the reaction of **1.16** by ^{1}H NMR spectroscopy

revealed the initial formation of a mono-carboxylate, mono-chloride ruthenium alkylidene species that slowly disappeared with appearance of pivalic acid. A C–H activated species with an intact benzylidene was subsequently observed, but this readily converted to a ruthenium hydride. X-ray crystallographic analysis of the resulting decomposition product revealed the novel η^2-bound olefin ruthenium complex **1.17** (Figure 7). Generation of pivalic acid suggested that C–H activation of the *N*-adamantyl substituent had occurred, but that the complex rapidly decomposed by a process involving alkylidene insertion and β-hydride elimination, as evidenced by the formation of a ruthenium hydride and the η^2-bound olefin motif found in the X-ray crystal structure of **1.17**. The formation of a ruthenium hydride via β-hydride elimination is further supported by observed olefin migration in cross metathesis reactions.[5]



Scheme 4: Decomposition product **1.17** derived from exposure of **1.16** to *t*-BuCOOAg (DIPP = 2,6-diisopropylphenyl).

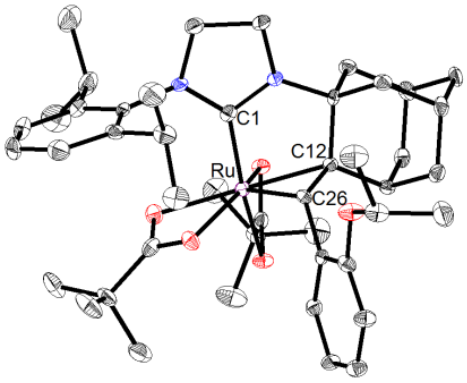
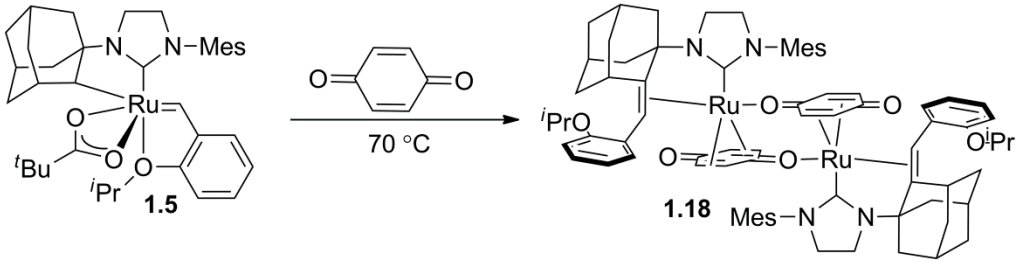


Figure 7: X-ray crystal structure of **1.17**. Displacement ellipsoids are drawn at 50% probability. For clarity, hydrogen atoms have been omitted. Selected bond lengths (Å) for **1.17**: C1-Ru 1.944, C12-Ru 2.130, C26-Ru 2.102, C12-C26 1.434.

Further evidence for β-hydride elimination playing a role in the decomposition of C–H activated catalysts was uncovered by treating catalyst **5** with *p*-benzoquinone (Scheme 5).[12] Addition of *p*-benzoquinone to **1.5** in C_6D_6 led to an immediate color change from purple to red/orange and decomposition of the original complex as evidenced by disappearance of the alkylidene resonance in the ^{1}H NMR spectrum. Crystals of the decomposition structure (**1.18**) were obtained and analysis by X-ray diffraction revealed the structure to be a ruthenium(0) dimer with η^2-bound olefins (Figure 8), a binding mode also observed for complex **1.17**, bridged by two benzoquinone ligands.



Scheme 5: Decomposition product **1.18** derived from exposure of **1.5** to excess *p*-benzoquinone.

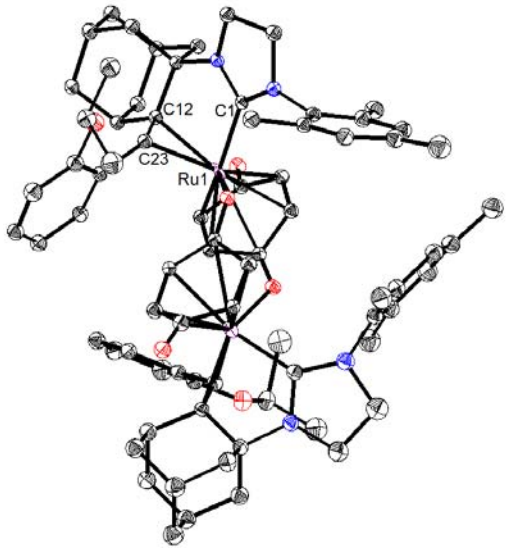
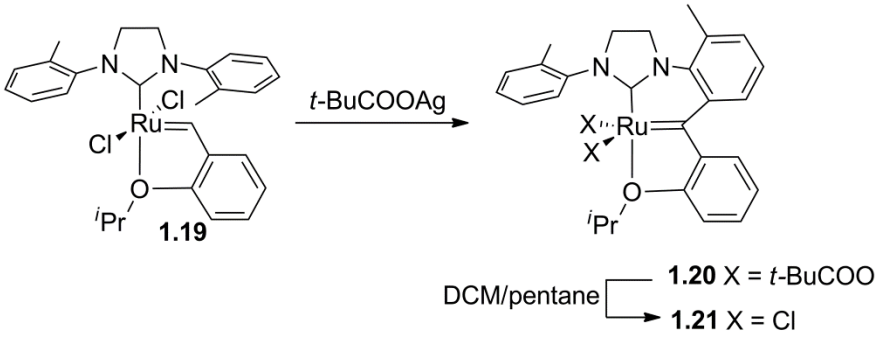


Figure 8: X-ray crystal structure of **1.18**. Displacement ellipsoids are drawn at 50% probability. For clarity, hydrogen atoms have been omitted. Selected bond lengths (Å) for **1.18**: C1-Ru 2.061, C12-Ru 2.245, C23-Ru 2.168, C12-C23 1.418.

The olefins of the benzoquinone ligands in **1.18** appear to be coordinated primarily in an η^4 fashion as demonstrated by the downfield ^{13}C carbonyl resonance (CD_2Cl_2, δ = 211.5 ppm), the relatively long C-O bond length (1.27 Å), and the boat-like conformation of the benzoquinone ligands.[13] Complexes similar to **1.18** have previously been observed for ruthenium and other metals,[14] although they are typically formed by simple ligand displacement. This novel structure appears to be the result of alkylidene insertion (as observed for complex **1.15**) and subsequent β-hydride elimination (as observed for **1.17**), reduction, and dimerization.

We next turned our attention to the synthesis of analogs of catalyst **1.5** with stronger ruthenium-carbon bonds derived from C–H activation of an sp^2-hybridized carbon-hydrogen bond,[15] and observed a unique decomposition mode seemingly resulting from alkylidene insertion and α-hydride elimination (Scheme 6). Complex **1.19**, a species containing hydrogen atoms at the *ortho*-position of its *N*-aryl substituents, immediately decomposed upon treatment with *t*-BuCOOAg, with appearance of pivalic acid and disappearance of the starting material's

alkylidene proton resonance, as observed by ^{1}H NMR spectroscopy. The resulting decomposition product (**1.21**) was crystallographically characterized and its structure revealed attachment of the benzylidene carbon to the *ortho* carbon of the *N*-aryl group, with retention of the alkylidene moiety (Figure 9).[16] Although mass spectrometry data of the initial product mixture suggested formation of **1.20**, upon prolonged treatment with a mixture of methylene chloride and pentane, the pivalate ligands were replaced by chlorides derived from the chlorinated solvent to yield **1.21**.[17] Observation of pivalic acid again suggested that a C–H activation event had occurred, but with subsequent decomposition. Attempted C–H activation of various other complexes containing *N*-aryl groups with unsubstituted *ortho*-positions resulted in this decomposition mode.



Scheme 6: Decomposition products **1.20** and **1.21** derived from exposure of **1.19** to *t*-BuCOOAg.

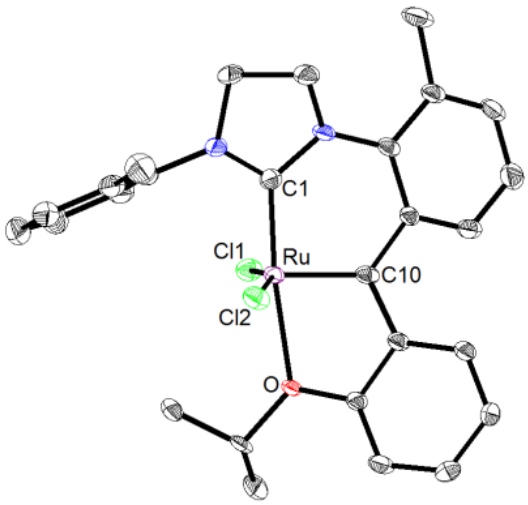
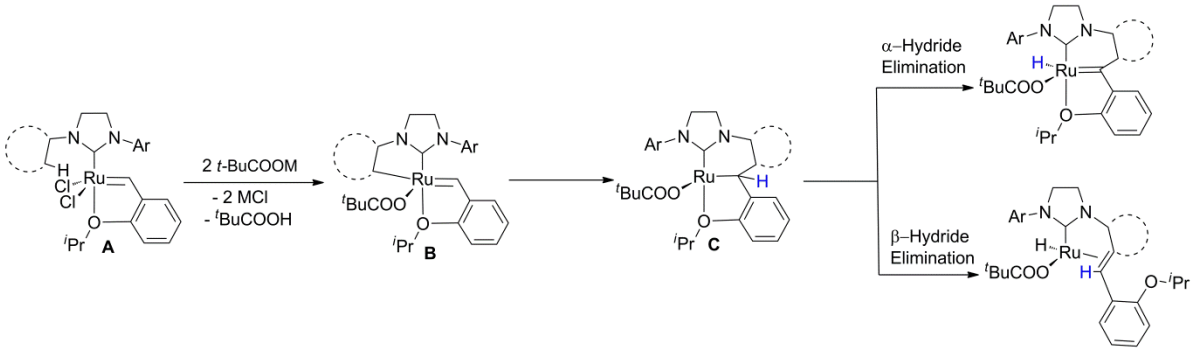


Figure 9: X-ray crystal structure of **1.21**. Displacement ellipsoids are drawn at 50% probability. For clarity, hydrogen atoms have been omitted. Selected bond lengths (Å) for **1.21**: C1-Ru 1.913, C10-Ru 1.829, Cl1-Ru 2.340, Cl2-Ru 2.341.

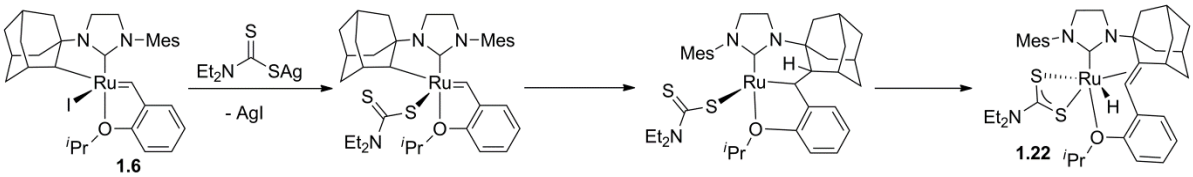
From the complexes presented above, we were able to elucidate a general decomposition mechanism for species related to complex **1.5** (Scheme 7). It is proposed that the unactivated catalysts **1.16** and **1.19**, upon treatment with *t*-BuCOOAg, form chelated architectures with an intact ruthenium alkylidene (**B**), as observed for catalyst **1.5**. However, these C–H activated species react further, as the alkylidene inserts into the newly formed ruthenium-carbon bond to yield alkyl ruthenium intermediate **C**. The isolated structure of complex **1.15** provides evidence for the *in situ* formation of this alkyl intermediate. Following insertion, the complex can undergo α– or β–hydride elimination to regenerate an alkylidene (as in **1.20** and **1.21**) or form an η^2-bound olefin complex (as in **1.17** and **1.18**), respectively.



Scheme 7: Proposed decomposition pathways for C–H activated ruthenium metathesis catalysts.

In these studies, the hydrides formed rapidly reacted with excess *t*-BuCOOAg to form the observed dipivalate adducts. The isolation and structural determination of ruthenium hydrides generated from chelated catalysts was highly desired. Accordingly, ruthenium-hydride **1.22** was formed by reaction of iodide-substituted catalyst **6** with silver (I) diethyldithiocarbamate, which

proceeded through alkylidene insertion and β-hydride elimination (Scheme 8). This species could be isolated and purified using column chromatography (SiO_2). The solid state structure of hydride **1.22** was determined using X-ray crystallography (Figure 10); this structure is closely related to dipivalate complex **1.17** that resulted from reaction of the corresponding hydride with excess *t*-BuCOOAg. In the more electron deficient hydride complex **1.22**, the isopropoxy group is bound to the Ru center, whereas in the dipivalate complex **1.17** the isopropoxy group is unbound.



Scheme 8: Proposed mechanism of formation of complex **1.22** from **1.6**.

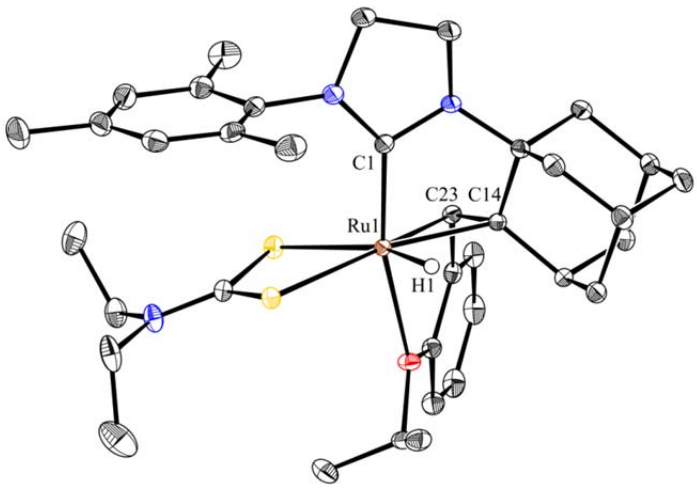
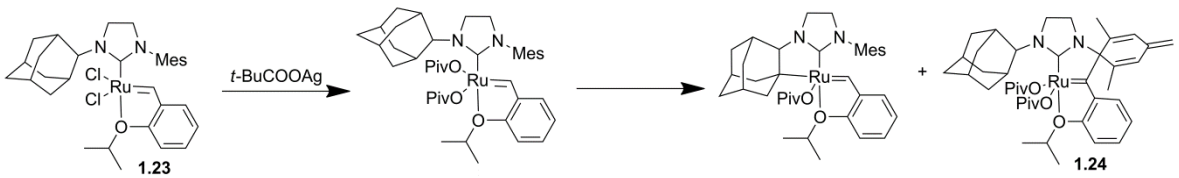


Figure 10: X-ray crystal structure of **1.22**. Displacement ellipsoids are drawn at 50% probability. For clarity, hydrogen atoms have been omitted. Selected bond lengths (Å) for **1.22**: C1-Ru1: 1.925, C14-Ru1: 2.113, C23-Ru1: 2.092, C14-C23: 1.440.

Over the course of subsequent studies, the decomposition of dipivalate intermediates was investigated. It has been shown that dipivalates are the species that undergo C–H activation;

mono chloride, mono carboxylate adducts have been independently prepared and do not undergo C–H activation even upon heating. As a result, studying the stability of dipivalate intermediates will allow us to better understand the mechanism of C–H activation. When complex **1.23** bearing an *N*-2-adamantyl group was treated with *t*-BuCOOAg, ligand exchange to form the corresponding dipivalate complex occurred and was observed by ^{1}H NMR spectroscopy (Scheme 9). A stable chelated complex was formed (*vide infra*) however another product (**1.24**) was concurrently formed and characterized by X-ray crystallography (Figure 11). In decomposition product **1.24**, the *N*-mesityl group had lost aromaticity and was converted to a *N*-1,4-cyclohexadienyl cycle, and ipso-carbon of the former *N*-mesityl group was bound to an intact alkylidene carbon. Additionally, H_2 gas was generated during the reaction. A proposed mechanism for this decomposition route is depicted in Scheme 10. Due to substitution with two bulky pivalate groups, the *N*-2-adamantyl group could be pushed farther away from the metal center, forcing the *N*-mesityl group close to the benzylidene. This proximity could enable attack of the electrophilic benzylidene carbon by the C=C bond of the *N*-mesityl group in a mechanism similar one seen in a Friedel-Crafts reaction. This would lead to a complex where the *ipso*-carbon of the former *N*-mesityl group is bound to the former benzylidene carbon. Additionally, the ruthenium center would be anionic and a tertiary carbocation would be formed on the *N*-substituent. The presence of this carbocation would increase the acidity of the *para*-methyl group due to resonance stabilization. Deprotonation using excess *t*-BuCOOAg would thus form a complex with the observed *N*-1,4-cyclohexadienyl group. A Subsequent α-hydride elimination and protonation of the Ru-H bond by *t*-BuCOOH would generate the observed product **1.24** and the byproduct H_2.



Scheme 9: Formation of decomposition product **1.24** from complex **1.23**.

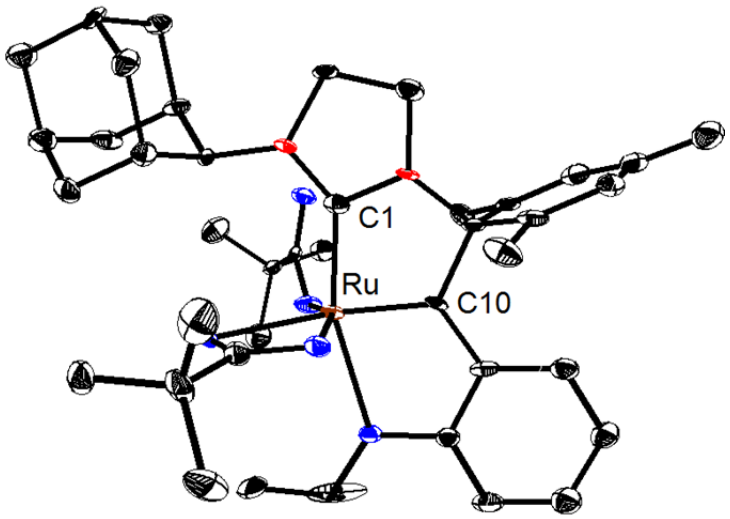
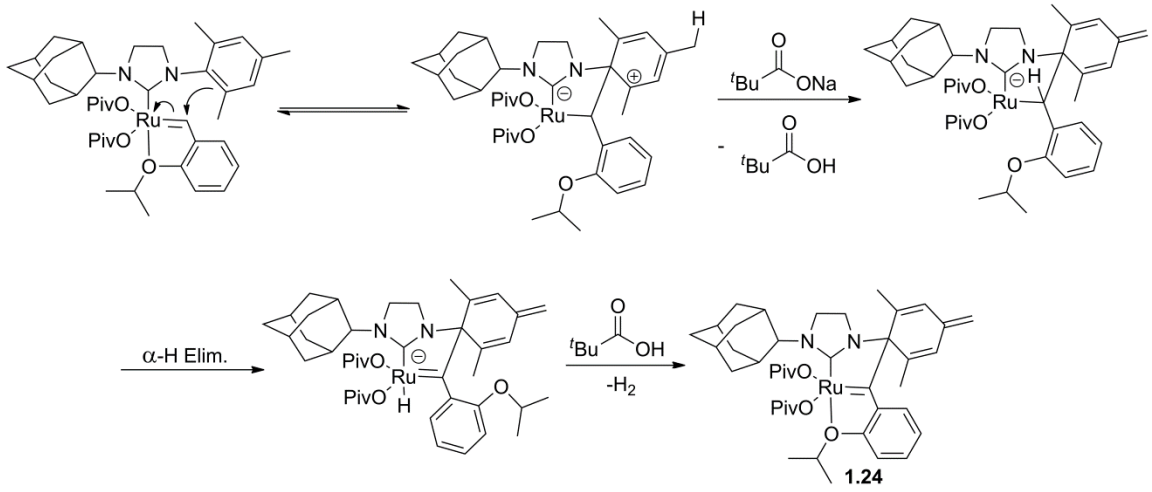


Figure 11: X-ray crystal structure of complex **1.24**. Displacement ellipsoids are drawn at 50% probability. For clarity, hydrogen atoms have been omitted. Selected bond lengths (Å) for **1.24**: C1-Ru: 1.94, C10-Ru: 1.84.



Scheme 10: Proposed decomposition pathway for the formation of complex **1.24**.

In an effort to probe the proposed decomposition mechanism for NHC-chelated complexes (Scheme 7), DFT calculation were performed on the decomposition modes of C–H activated catalyst **1.5**. Both α- and β-hydride elimination pathways were investigated and the free energy profile is shown in Figure 12. Energies were calculated in the gas phase using M06 and with a mixed basis set of SDD for ruthenium and 6-311+G(d,p) for other atoms; B3LYP energies are also given in Figure 12. Geometries were optimized with B3LYP/LANL2DZ–6-31G(d), and all calculations were performed with Gaussian 09.[18] Based on these computational results, the decomposition of NHC-chelated catalysts initiates by alkylidene insertion into the chelating ruthenium-carbon bond as proposed.

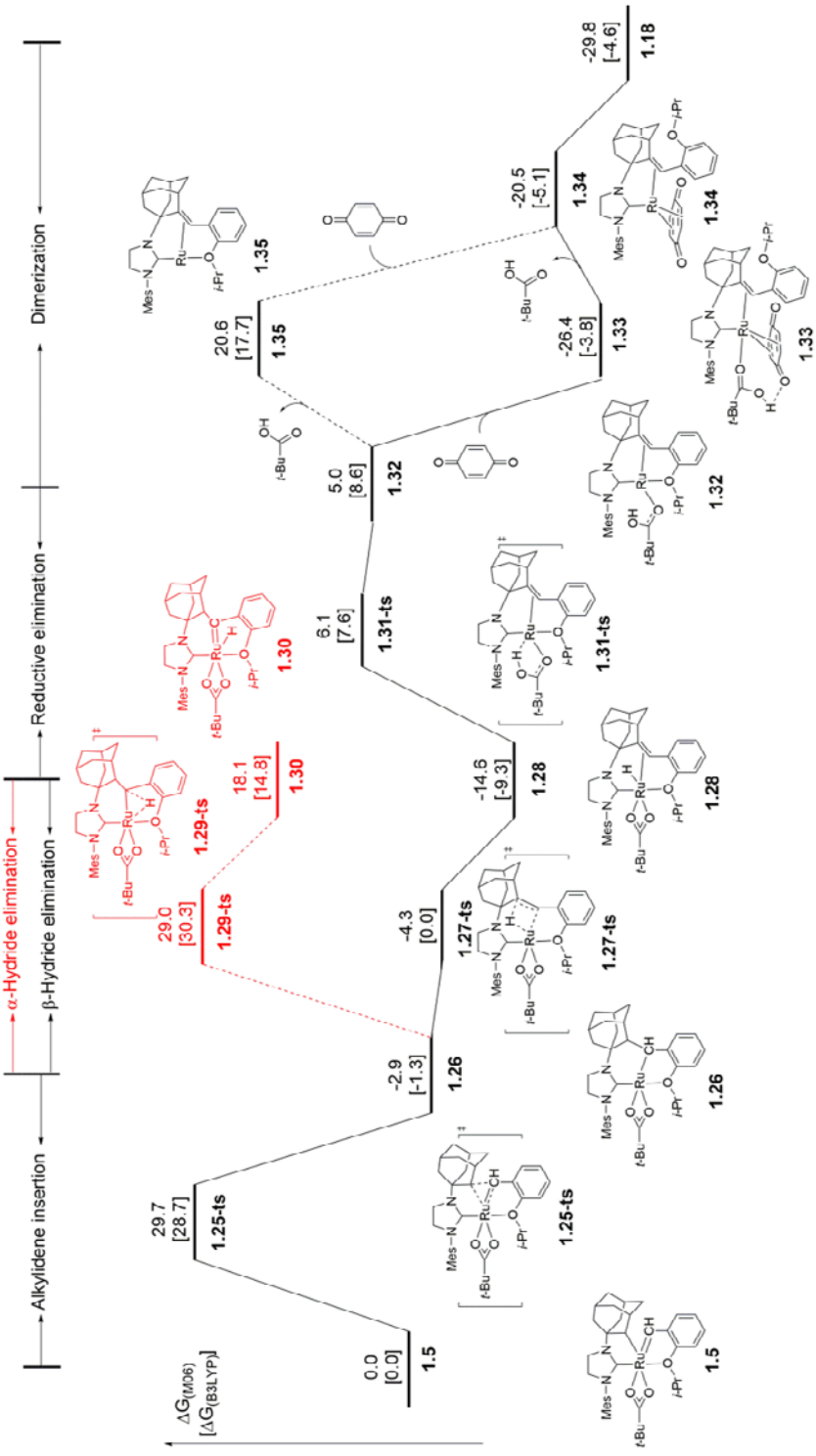


Figure 12: The free energy profile of the decomposition pathways for C–H activated ruthenium catalyst **1.5**. The values are relative free energies calculated by M06 and B3LYP (in square brackets) and given in kcal/mol. B3LYP was used in the geometry optimizations.

The decomposition of catalyst **1.5** initiates via insertion of the alkylidene into the ruthenium-carbon (adamantyl) bond (**1.25-ts**), for which both M06 and B3LYP predicted an activation barrier of ~29 kcal/mol. The alkylidene insertion leads to alkyl ruthenium complex **1.26**, a structure similar to proposed intermediate **C** in Scheme 6. β-Hydride elimination from **1.26** is facile (**1.27-ts**),[19] while the activation barrier for α-hydride elimination (**1.29-ts**) is calculated to be 33.3 kcal/mol higher. This β-hydride elimination reaction leads to ruthenium hydride intermediate **1.28** which is 14.6 kcal/mol more stable than catalyst **1.5**. These energy differences agree well with previous experimental observations of ruthenium-hydride species by ^{1}H NMR. The overall exergonicity of the transformation from **1.5** to **1.28** suggests that the alkylidene insertion is irreversible.

The preference for β-hydride elimination over α-hydride elimination agrees with the observed decomposition product derived from complex **1.17** (Scheme 4). Previous experimental and theoretical studies performed on hydride elimination reactions of ruthenium pincer-type complexes analogous to intermediate **C** also suggest that when α– and β–hydrogens are both present, β–hydride elimination is energetically favored, however when the molecule lacks β–hydrogens, α-hydride elimination occurs.[20] This is the case for the alkyl intermediate (**C**) of complex **6** resulting from C–H activation and alkylidene insertion, as its backbone does not contain β-hydrogens, and thus only α–hydride elimination can occur and is therefore observed. The ruthenium-hydride species (analogs of **1.28** and **1.30**) generated from these hydride elimination reactions subsequently react with the excess *t*-BuCOOAg to generate **1.17** and **1.20**, respectively.[21]

The transformation from **1.28** to the dimeric complex **1.18** was also investigated using DFT and the free energy profile is shown in Figure 12. Reductive elimination of pivalic acid from ruthenium hydride **1.28** forms a ruthenium (0) complex **1.32**, which is 19.6 kcal/mol less stable

than complex **1.28**.[22] Subsequent ligand exchange replaces the pivalic acid with benzoquinone and forms the ruthenium(0) complex **1.34**, in which the benzoquinone is η^4-coordinated with ruthenium; the benzoquinone binds to the ruthenium much more strongly than pivalic acid. M06 predicted that the ruthenium(0)-benzoquinone complex **1.34** is 25.5 kcal/mol more stable than the ruthenium(0)-pivalic acid complex **1.14**, while B3LYP predicted that **1.16** is only 15.7 kcal/mol more stable than **1.32**. The energy differences between B3LYP and M06 here are not unexpected, since B3LYP is known to underestimate the binding energy of olefins to ruthenium centers.[23] The ligand exchange from **1.32** to **1.34** occurs via an associative pathway involving complex **1.33**, as the dissociative ligand exchange pathway would involve generating the unstable 14 electron complex **1.35** and thus is predicted to be less favorable. The electron-deficient C=C bonds in *p*-benzoquinone bind strongly with the π-basic zero-valent ruthenium in complexes **1.33** and **1.34**.[24] Dimerization of complex **1.34** leads to the crystallographically characterized ruthenium dimer complex **1.18** and this dimerization is exergonic by 9.4 kcal/mol. Addition of benzoquinone facilitates the decomposition of ruthenium hydride **1.28** by stabilizing the ruthenium(0) species that leads to formation of the stable dimeric complex **1.18**. The increased decomposition rate with addition of benzoquinone suggests that this additive may also accelerate alkylidene insertion (**1.25-ts**), however the mechanism of this process is not clear.

In conclusion, we have investigated the decomposition of a new class of *Z*-selective metathesis catalysts with chelating NHC ligands resulting from an initial carboxylate-driven C–H bond insertion. Formation of a stable carbon-ruthenium bond in the presence of an alkylidene seems to be subtly dependent on a variety of steric and electronic factors. A number of decomposition products derived from side reactions of C–H inserted complexes were characterized by X-ray crystallography and from these, decomposition pathways were proposed. The decomposition of C–H activated catalysts is thought to proceed via insertion of the chelating ruthenium-carbon bond into the alkylidene to yield an alkyl ruthenium intermediate. Due to the

presence of a vacant coordination site, subsequent hydride elimination can occur in these alkyl intermediates to generate a ruthenium hydride, which has been proposed to cause olefin migration of alkene substrates. Density functional theory calculations were performed and support the proposed decomposition pathway of **1.5,** which proceeds via insertion of the alkylidene into the chelating ruthenium-carbon bond and subsequent β-hydride elimination, leading to a ruthenium hydride complex.

The decomposition modes presented above are markedly distinct from those observed for previous generations of ruthenium metathesis catalysts. Preventing alkylidene insertion and hydride elimination will be key criteria in future catalyst development. In spite of these decomposition modes, such chelated complexes have proven to be effective catalysts for *Z*-selective olefin metathesis. Since decomposition can reduce overall catalyst activity and enable undesired side reactions, designing more stable catalysts by understanding catalyst decomposition is essential for highly chemoselective metathesis reactions.

SODIUM PIVALATE METHOD:

Synthesizing new NHC-chelated architectures with differing NHC substituents has proven difficult and mostly results in decomposition after exposure to *t*-BuCOOAg. The *N*-1-adamantyl group of **1.5** is unique in that the bond that undergoes C–H activation on the preactivated species (**1.4**) is quite close to the ruthenium center (2.80 Å). This led to a complex that was seemingly less susceptible to insertion of the ruthenium-carbon bond into the alkylidene and subsequent decomposition. As previously mentioned, retaining this adamantyl group and exchanging the *N*-mesityl group for an *N*-2,6-diisopropylphenyl group (**1.16**) led to mostly decomposition after exposure to *t*-BuCOOAg (Scheme 4).

The use of *t*-BuCOOAg to cause the ligand exchange of chlorides for carboxylates was undesired because an excess amount of this reagent was shown to induce the decomposition of

otherwise stable chelated complexes. If this salt metathesis step was slow for a particular catalyst, the C–H activated species would decompose before it could be isolated. We thus sought to find conditions that used a less reactive, cheap metal to cause the ligand exchange. After screening a number of alkali metal derivatives and reaction conditions, it was discovered that exposing the unactivated catalyst **1.4** to sodium pivalate (*t*-BuCOONa) in a 1:1 mixture of MeOH and THF led to clean formation of the desired chelated catalyst **1.5** after heating at 40 °C overnight.[25] Using *t*-BuCOONa to effect the salt metathesis and C–H activation, complex **1.11** was synthesized in two steps with 60% overall yield; this is in contrast to the analogous route using *t*-BuCOOAg that proceeded in 48% overall yield. Additionally, sodium acetate could be employed to form acetate-substituted catalyst **1.8** directly from **1.4**. In order to show the utility and mildness of this new approach, we sought to synthesis catalyst **1.35** which had decomposed *in situ* when prepared with *t*-BuCOOAg. Indeed we were able to cleanly form stable chelated catalyst **1.35** after heating for 6 days at 40 °C (Figures 13 and 14). Catalyst **1.35** has emerged as the most active and *Z*-selective metathesis catalyst to date, exhibiting up to 7400 turnovers in homodimerization reactions and near perfect *Z*-selectivity (>98%) in mostly all metathesis reaction attempted.

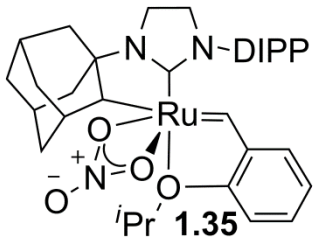


Figure 13: Highly active and *Z*-selective ruthenium catalyst **1.35** bearing an *N*-DIPP group.

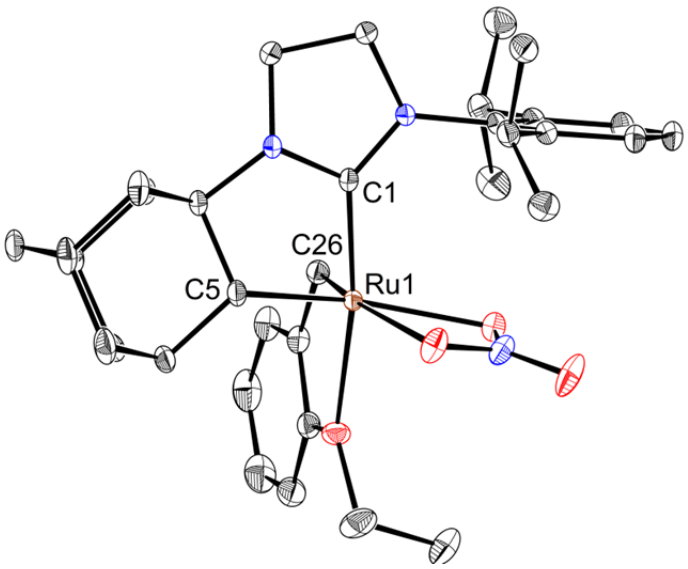


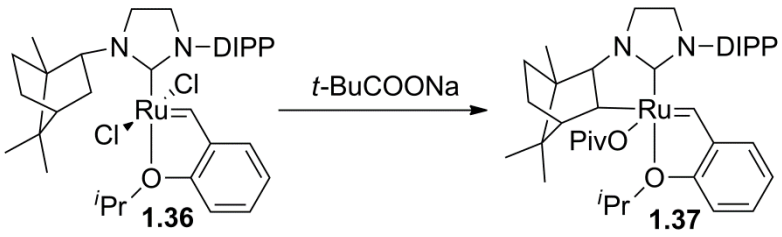
Figure 14: X-ray crystal structure of **1.35**. Displacement ellipsoids are drawn at 50% probability. For clarity, hydrogen atoms have been omitted. Selected bond lengths (Å) for **1.35**: C1-Ru1: 1.95, C5-Ru1: 2.06, C26-Ru1: 1.85.

DEVELOPMENT OF NEW CHELATES:

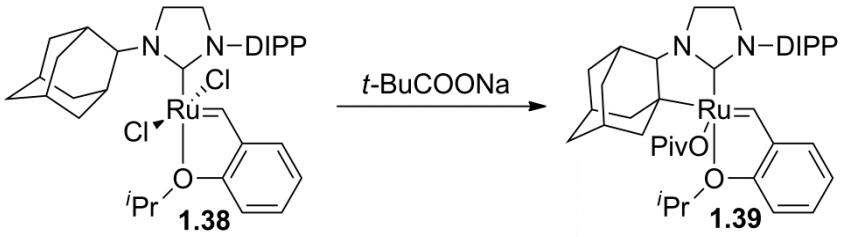
Discovery of a milder method for salt metathesis and C–H activation has allowed for the preparation of catalysts with chelating *N*-substituents different than *N*-1-adamantyl that were previously not possible. This has allowed insight into how other chelating substituents affect stability and activity of the resulting catalysts. Due to the unpredictable stability of C–H activated architectures, we first sought to screen a number of metathesis catalysts to determine if a stable ruthenium-carbon bond could be formed after a carboxylate-driven C–H bond insertion. A number of ruthenium catalysts were prepared with alternative *N*-carbocyclic chelating groups, and changes to the NHC ligand. The starting material dichloride catalysts were synthesized through straightforward ligand and catalyst synthesis, and were subsequently tested for their ability to form a stable chelating ruthenium-carbon bond in the presence of an alkylidene, by ^{1}H NMR spectroscopy. Ten equivalents of sodium pivalate (*t*-BuCOONa) were added to a solution

of each catalyst in a 1:1 mixture of CD_3OD and THF-d_8. With species that were able to form a stable chelated complex, the starting material was readily converted to a NHC-chelated species with concurrent generation of pivalic acid. Alternatively, with some species, a dicarboxylate complex resulting from salt metathesis of the starting complex was distinctly observed before C–H activation occurred. If pivalic acid was generated with disappearance of the starting material dichloride complex or the analogous dicarboxylate adduct, with formation of a ruthenium-hydride, the complex was deemed unstable and not relevant for further study. We scaled up the synthesis of complexes observed to form a stable chelated architecture using previously described methods.

Ruthenium dichloride complex **1.36**, bearing an *N*-bornyl group,[26] and complex **1.38**, bearing an *N*-2-adamantyl group, were prepared and treated with *t*-BuCOONa. Formation of the desired five-membered chelates derived from a carboxylate-assisted C–H activation of the corresponding *N*-carbocycle group was monitored by ^{1}H NMR spectroscopy. For both **1.36** and **1.38**, the dipivalate intermediates were initially observed followed by clean formation of the desired chelated products **1.37** and **1.39**, respectively (Schemes 11 and 12); the assumed connectivity is depicted below, but has yet to be confirmed by NMR spectroscopy and X-ray crystallography analysis. Complex **1.37** bears a chiral chelating *N*-bornyl group and thus could find utility in enantioselective metathesis reactions. Both **1.37** and **1.39**, however, have yet to be evaluated in metathesis reactions.

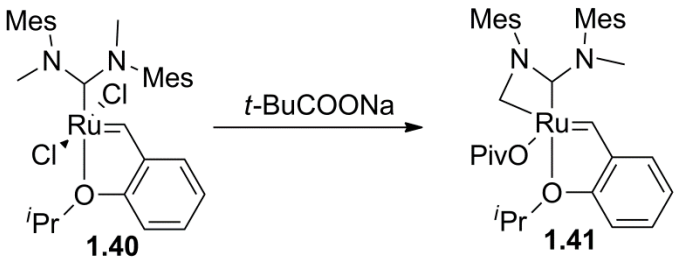


Scheme 11: Synthesis of *N*-bornyl activated complex **1.37**.



Scheme 12: Synthesis of *N*-2-adamantyl activated complex **1.39**.

Previously reported complex **1.40**, bearing an acyclic diamino carbene, was treated with *t*-BuCOONa with the expectation that the *N*-mesityl group would be activated to form a six-membered chelating architecture.[27] However, the *N*-methyl group was alternatively activated and a four-membered chelate was formed (**1.41**) (Scheme 13); this marked the first time a four-membered chelate had been observed with these types of ruthenium alkylidene complexes and this unique structure was verified by X-ray crystallographic analysis (Figure 15). In the crystal structure of the unactivated complex **1.40**, the distance between the methyl group that is activated and the Ru center is quite short (2.83 Å) which helps explain why a four-membered chelate would form as opposed to a six-membered chelate. The stability of this chelated complex is seemingly due to the flexibility of the acyclic diamino carbene. Complex **1.41** was evaluated in olefin homodimerization reactions, but was not active even upon heating. It was able to react with norbornene in a ring-opening metathesis polymerization (ROMP) reaction, however the yield was low.



Scheme 13: Synthesis of complex **1.41** bearing a four-membered chelate.

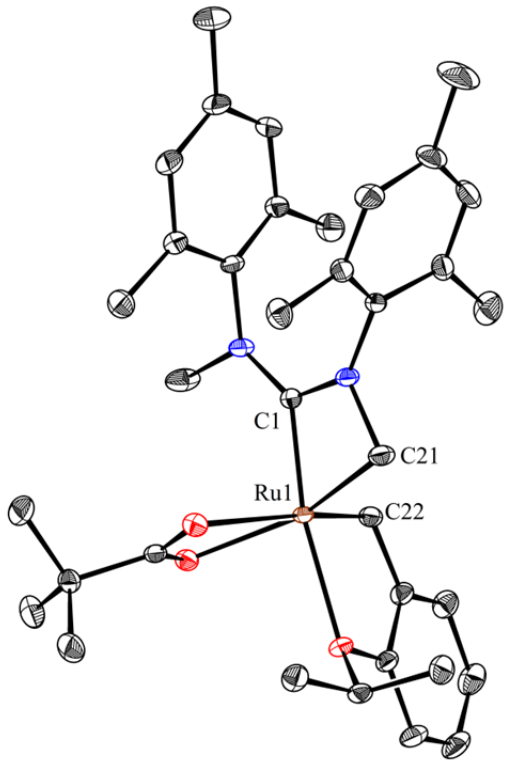
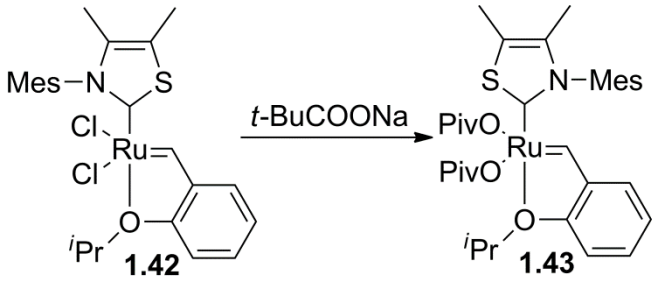


Figure 15: X-ray crystal structure of **1.41**. Displacement ellipsoids are drawn at 50% probability. For clarity, hydrogen atoms have been omitted. Selected bond lengths (Å) for **1.41**: C1-Ru1: 1.96, C21-Ru1: 2.07, C22-Ru1: 1.85.

During our investigations into developing new chelating groups, we were able to isolate stable pivalate intermediates that unexpectedly did not undergo C–H activation. Studying these types of intermediates could provide important insight into the mechanism of carboxylate-assisted C–H activation and why certain groups cannot be activated. Previously reported complex **1.42** was treated with *t*-BuCOONa in hopes that a six-membered chelating architecture would be generated (Scheme 14).[28] However, the corresponding dipivalate-substituted complex **1.43** was formed according to ^{1}H NMR spectroscopy. A crystal structure of complex **1.43** was obtained and provided insight into why this complex did not undergo C–H activation (Figure 16). In the structure of the starting complex **1.42**, the *N*-mesityl group resides over the chloride X-type

ligands. In the structure of **1.43**, however, the NHC has rotated and the *N*-mesityl group resides over the ruthenium alkylidene, most likely due to the increased steric bulk of the pivalate X-type ligands. As a result, the *ortho*-methyl group of the *N*-mesityl group is too far from the pivalate ligands to undergo a carboxylate-assisted activation. Similarly, when activation was attempted on complex **1.44**, bearing an *N*-benzyl group, a dipivalate-substituted complex was formed (Scheme 15). The product was crystallographically characterized and revealed that the *N*-benzyl group was located too far from the pivalate ligands to readily undergo C–H activation (Figure 17). It seems that adding a methylene linker to an *N*-substituent gives the group added flexibility, allowing it to rotate away from the bulky pivalates and avoid C–H activation. The information gained from isolation and characterization of dipivalate-substituted complexes **1.43** and **1.45** will be important for the future design of chelated alkylidene complexes for *Z*-selective olefin metathesis transformations.



Scheme 14: Formation of stable dipivalate-substituted complex **1.43**.

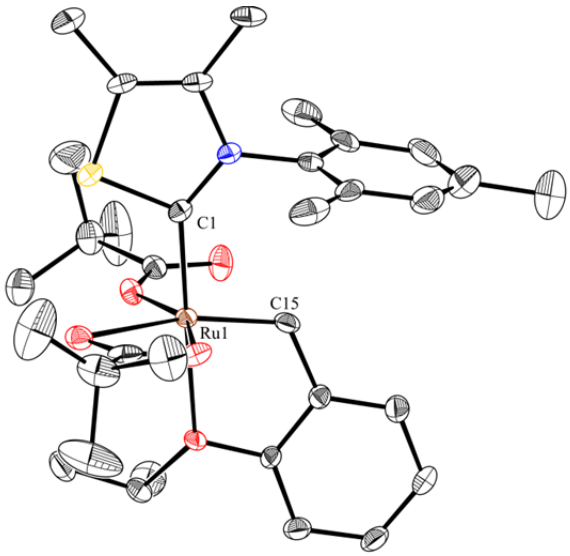
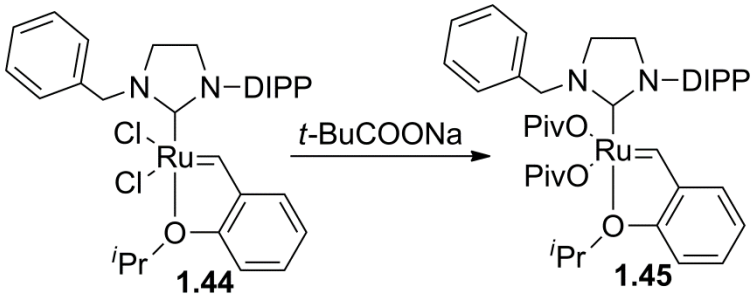


Figure 16: X-ray crystal structure of **1.43**. Displacement ellipsoids are drawn at 50% probability. For clarity, hydrogen atoms have been omitted. Selected bond lengths (Å) for **1.43**: C1-Ru1: 1.97, C15-Ru1: 1.84.



Scheme 15: Formation of stable dipivalate-substituted complex **1.45**.

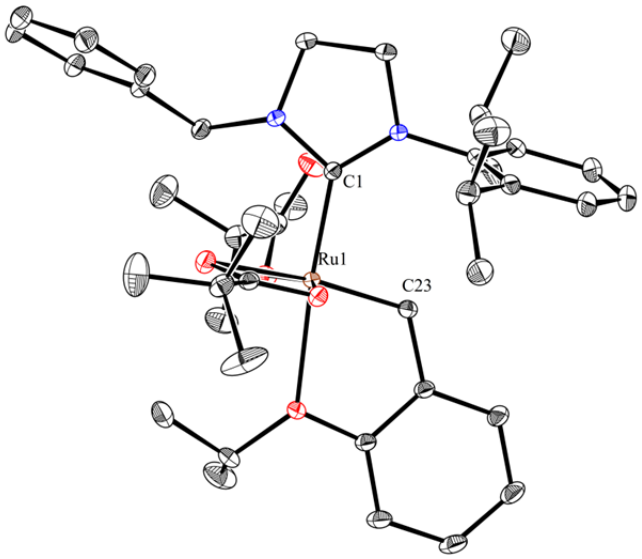


Figure 17: X-ray crystal structure of **1.45**. Displacement ellipsoids are drawn at 50% probability. For clarity, hydrogen atoms have been omitted. Selected bond lengths (Å) for **1.45**: C1-Ru1: 1.97, C23-Ru1: 1.84.

CONCLUSIONS:

The serendipitous discovery that NHC chelated ruthenium alkylidene complexes could be stably formed and exhibited high *Z*-selectivity in olefin metathesis reactions has enabled the development of ever more active and selective catalysts. In order to design catalysts with more stable chelating architectures, the decomposition of chelated catalysts was investigated using experimental and theoretical techniques. It was found that decomposition proceeds via irreversible insertion of the alkylidene into the chelating ruthenium carbon bond to generate a ruthenium alkyl intermediate that contains an open coordination site. Depending on the presence or absence of a β-proton, either an α- or β-hydride elimination can occur to generate the corresponding hydrides; it was found that β-hydride elimination is energetically more favorable. These decomposition modes were elucidated by the isolation and crystallographic characterization of a number of decomposition products, including a ruthenium hydride. Results

also suggested that the silver (I) reagents used to effect the salt metathesis and C-H activation were enabling the decomposition modes outlined above and thus a more mild method, using sodium carboxylates, was developed.

This method has allowed a large number of new and improved catalysts to be accessed for the first time. Notably, a catalyst (**1.35**) was discovered that exhibited near perfect *Z*-selectivity (>98%) in a variety of olefin metathesis reactions and with high activity (up to 7400 turnovers). More recently, the synthesis of catalysts with new chelating architectures has been achieved. For example, different carbocyclic groups, including *N*-bornyl (**1.37**) and *N*-2-adamantyl (**1.39**), have shown to undergo clean C-H activation to form new five-membered chelating catalysts. Additionally, the methyl group of an acyclic diamino carbene has been shown to undergo C-H activation to form a four-membered chelating architecture (**1.41**), which had previously not been observed. The studies into the stability and decomposition of NHC-chelated ruthenium alkylidene catalysts presented here have enabled the discovery of highly active catalysts that are now capable of producing *Z*-internal olefins with only trace amounts of the undesired *E*-isomer.

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19. Both B3LYP and M06 predicted very low barriers for β-hydride elimination. B3LYP predicted the barrier from **1.26** to **1.27-ts** to be 1.3 kcal/mol. M06 single point calculations with B3LYP geometries resulted in a small negative barrier, due to the different locations of saddle point on M06 and B3LYP surfaces (Figure 12).

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21. It is proposed that these ruthenium hydrides react with *t*-BuCOOAg to produce an ill-defined mixture of silver (I) hydrides. All attempts to observe such species by 1H NMR were unsuccessful due to insolubility of the resulting gray precipitate in deuterated solvents.

22. Pivalic acid generation is observed by ^{1}H NMR spectroscopy after the addition of *p*-benzoquinone to complex **1.5**.

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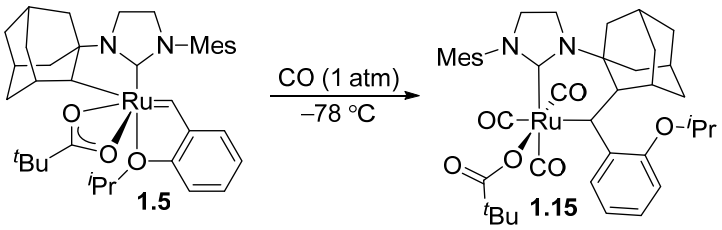
Experimental Section:

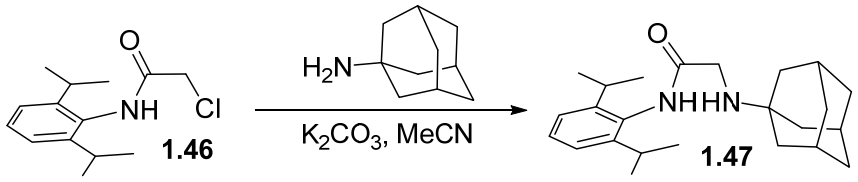
General Information

All reactions were carried out in dry glassware under an argon atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres Glovebox under a nitrogen atmosphere unless otherwise specified. All solvents were purified by passage through solvent purification columns and further degassed by bubbling argon. Hexane was dried over CaH_2 and distilled into a dry Schlenk flask and subsequently degassed with argon. NMR solvents were dried over CaH_2 and vacuum transferred to a dry Schlenk flask and subsequently degassed with bubbling argon. C_6D_6 was purified by passage through a solvent purification column. $CDCl_3$ was used as received. Potassium *t*-amyloxide was purchased as a toluene solution and concentrated before use. Dichloro(*o*-isopropoxyphenylmethylene) (tricyclohexylphosphine) ruthenium was obtained from Materia, Inc. **1.1**, 2-chloro-N-2,6-diisopropylphenylacetamide,[29] **1.36**,[26] **1.40**,[27] and **1.42**[28] were synthesized according to previous reports. Other commercially available reagents and silica gel were used as received.

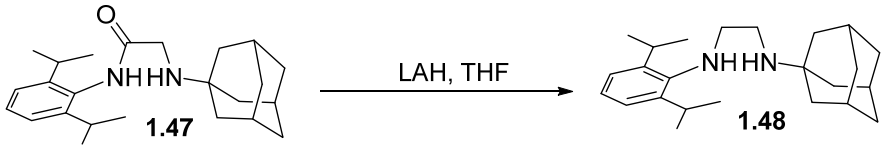
^1H and ^{13}C NMR spectra were recorded on a Varian 600 MHz spectrometer, Varian 500 MHz spectrometer, or a Varian 400 MHz spectrometer. High-resolution mass spectra were provided by the California Institute of Technology Mass Spectrometry Facility using a JEOL JMS-600H High Resolution Mass Spectrometer. X-ray crystallographic data was collected by the California Institute of Technology Beckman Institute X-ray Crystallographic Facility using Bruker KAPPA APEXII X-ray diffractometer.



Synthesis of 1.15: In a glovebox, a Schlenk flask was charged with **1.5** (26 mg, 0.039 mmol) and THF (1 mL). The reaction was removed from the glovebox, attached to a vacuum manifold, and cooled to –78 °C in a CO_2/acetone bath. The flask was evacuated and ca. 1 atm of CO was added through the vacuum manifold and the reaction was allowed to stir for 15 min at −78 °C under a continuous stream of CO. During this time, the color of the solution changed from purple to light gray. After the elapsed time, the reaction was concentrated and placed back in the glovebox where it was dissolved in C_6H_6, transferred to a 20 mL vial, and concentrated a second time to give **1.15** as a yellow solid (28 mg, 93%). Crystals suitable for X-ray diffraction were grown from slow diffusion of pentane into a saturated toluene solution. ^{1}H NMR (400 MHz, C_6D_6) δ 7.66 (d, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.91 (dt, *J* = 7.2, 1.8 Hz, 1H), 6.72 (s, 1H), 6.70 – 6.60 (m, 2H), 4.41 (sept, *J* = 6.1 Hz, 1H), 4.15 (d, *J* = 11.8 Hz, 1H), 3.83 (d, *J* = 12.4 Hz, 1H), 3.18 – 3.04 (m, 1H), 3.03 – 2.86 (m, 2H), 2.83 – 2.71 (m, 1H), 2.69 – 2.59 (m, 1H), 2.32 – 2.23 (m, 1H), 2.12 (s, 2H), 2.05 (s, 6H), 1.99 (br s, 3H), 1.92 – 1.83 (m, 2H), 1.79 – 1.71 (m, 1H), 1.70 – 1.64 (m, 1H), 1.62 (s, 9H), 1.58 – 1.50 (m, 2H), 1.48 – 1.44 (m, 1H), 1.31 (d, *J* = 6.0 Hz, 3H), 1.29 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 201.38, 199.70, 188.49, 184.68, 182.09, 150.91, 147.97, 139.48, 138.44, 138.38, 136.02, 123.27, 120.53, 111.37, 67.98, 67.84, 61.76, 49.42, 45.60, 44.92, 44.40, 38.36, 37.21, 36.32, 31.57, 30.40, 30.26, 30.08, 29.65, 25.84, 22.52, 21.97, 21.02, 18.34, 17.98, 17.67. HRMS (FAB+): M – (-O-(CH)$(CH_3)_2$) Calculated – 700.2451, Found – 700.2458.

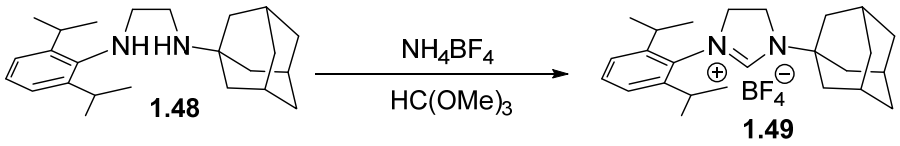


Synthesis of 1.47: **1.46** (2.90 g, 11.43 mmol), 1-adamantylamine (3.46 g, 22.9 mmol), and anhydrous potassium carbonate (3.17 g, 22.9 mmol) were added to a 250 mL round bottom flask with MeCN (120 mL) and heated to reflux for 28 h. After cooling to room temperature, the solution was filtered and concentrated *in vacuo*. The crude mixture was chromatographed through silica gel with a mobile phase of CH_2Cl_2 and THF (4:1). The solvent was removed *in vacuo* and **1.47** was obtained as a white solid (7.02 g, 61%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.07 (s, 1H), 7.19 - 7.29 (m, 1H), 7.19 (d, *J* = 7.7 Hz, 2H), 3.46 (s, 2H), 3.04 (sept, *J* = 6.9 Hz, 2H), 2.13 (s, 3H), 1.70 (dd, *J* = 15.3, 7.5 Hz, 9H), 1.63 (d, *J* = 11.7 Hz, 3H), 1.22 (d, *J* = 6.9 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.56, 145.92, 131.78, 128.14, 123.63, 51.33, 44.31, 43.14, 36.74, 29.71, 29.09, 23.84. HRMS (FAB+): Calculated – 369.2906 Found – 369.2893.

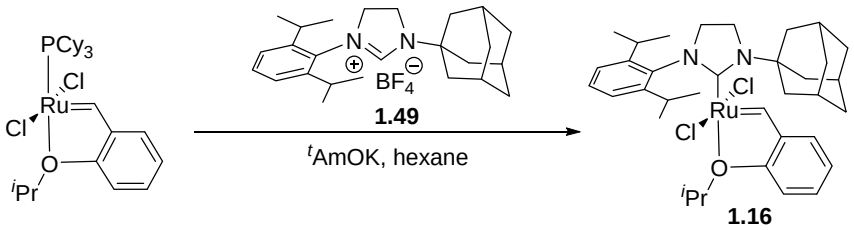


Synthesis of 1.48: **1.47** (2.47 g, 6.69 mmol) was added to a 100 mL three-necked round bottom flask containing THF (60 mL). Lithium aluminum hydride (2.10 g, 55.3 mmol) was added slowly and the mixture was refluxed for 16 h. The flask was cooled to 0 °C in an ice bath. Water (1.5 mL), a 2N NaOH solution (3 mL), and water (3 mL) were added sequentially. Et_2O (30 mL) and water (30 mL) were added and the solution was allowed to stir for 1 h at room temperature. The mixture was poured into a separatory funnel, the organic phase was collected and the aqueous phase was extracted with Et_2O (2 x 30 mL). The organic phases were combined and washed with

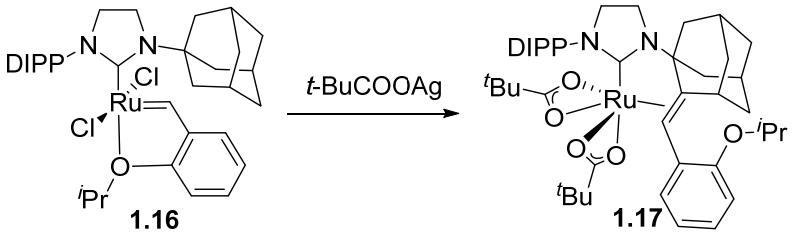
water (3 x 30 mL), a saturated sodium chloride solution (1 x 30 mL), and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* to yield **1.48** as a yellow solid (2.00 g, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 - 7.02 (m, 3H), 3.38 (sept, *J* = 6.8 Hz, 2H), 2.97 (dd, *J* = 6.6, 4.8 Hz, 2H), 2.88 (dd, *J* = 6.6, 4.7 Hz, 2H), 2.11 (s, 3H), 1.75-1.62 (m, 12H), 1.27 (d, *J* = 6.9 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.08, 142.27, 123.53, 123.38, 52.74, 50.35, 43.24, 40.78, 36.94, 29.76, 27.69, 24.36. HRMS (FAB+): Calculated – 355.3113 Found – 355.3104.



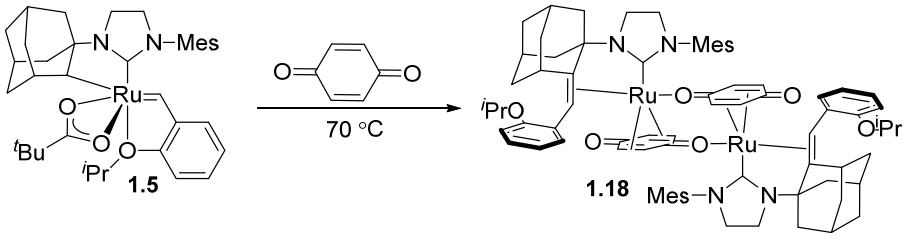
Synthesis of 1.49: **1.48** (1.47 g, 4.13 mmol) was added to a 25 mL three-necked flask with NH_4BF_4 (467 mg, 4.54 mmol) and trimethylorthoformate (15 mL). The suspension was refluxed for 2 h and the solvent was evaporated. The crude product was washed with a mixture of toluene and isobutanol (1:1), then hexane. After drying under high vacuum, **1.49** was obtained as a white solid (759 mg, 41%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 4.34 (dd, *J* = 12.8, 9.4 Hz, 2H), 4.23-4.17 (m, 2H), 2.86 (sept, *J* = 6.8 Hz, 2H), 2.22 (s, 3H), 2.01 (d, *J* = 3.2 Hz, 6H), 1.71 (t, *J* = 3.1 Hz, 6H), 1.24 (dd, *J* = 25.4, 6.8 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.05, 146.82, 131.12, 130.56, 124.96, 58.13, 53.26, 45.21, 35.53, 29.33, 28.82, 24.88, 24.29. HRMS (FAB+): Calculated – 365.2957 Found – 365.2949.



Synthesis of 1.16: In a glovebox, **1.49** (250 mg, 0.553 mmol), potassium *t*-amyloxide (73.3 mg, 0.581 mmol) and hexane (15 ml) were placed in a 50 ml Schlenk flask. After stirring at room temperature for 1 h, dichloro(*o*-isopropoxyphenylmethylene) (tricyclohexylphosphine) ruthenium (315.3 mg, 0.525 mmol) was added. The dark red-brown solution was stirred at 65 °C for 4 h, during which time a green precipitate formed. After cooling to room temperature, the green solid was collected by filtration and washed with hexane (20 ml x 3 times). The resulting solid was extracted with CH_2Cl_2 and the solvent was removed *in vacuo*. After drying under high vacuum, **1.16** was obtained as air-stable bright green solid (342 mg, 90%). ^{1}H NMR (500 MHz, C_6D_6) δ 17.23 (s, 1H), 7.42-7.35 (m, 1H), 7.27 (s, 1H), 7.26 (s, 1H), 7.20-7.17 (m, 1H), 7.09 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.69 (td, *J* = 7.4, 0.8 Hz, 1H), 6.45 (d, *J* = 8.5 Hz, 1H), 4.61-4.49 (m, 1H), 3.55-3.48 (m, 2H), 3.45 (dd, *J* = 13.6, 6.8 Hz, 2H), 3.36 (dd, *J* = 11.5, 8.5 Hz, 2H), 2.96 (s, 6H), 2.29 (s, 3H), 1.89 (d, *J* = 12.0 Hz, 3H), 1.67 (d, *J* = 12.4 Hz, 3H), 1.57 (d, *J* = 6.1 Hz, 6H), 1.15 (dd, *J* = 9.8, 6.8 Hz, 12H). ^{13}C NMR (126 MHz, C_6D_6) δ 303.67, 252.87, 210.71, 153.20, 148.69, 145.61, 140.34, 129.96, 129.52, 125.30, 123.42, 122.57, 113.57, 74.26, 57.39, 54.68, 44.18, 42.42, 36.38, 30.52, 28.25, 25.91, 24.56, 22.57. HRMS (FAB+): Calculated – 684.2188, Found – 684.2217.



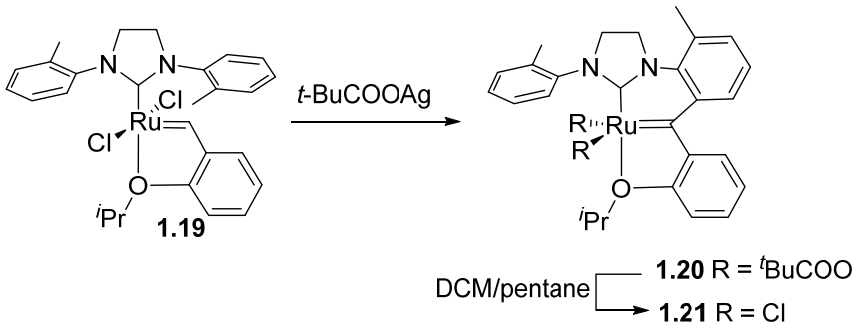
Synthesis of 1.17: In a glovebox, a 20 mL vial was charged with **1.16** (100 mg, 0.146 mmol), *t*-BuCOOAg (153 mg, 0.730 mmol) and THF (5 mL). The mixture was stirred at room temperature in the dark for 4 h. The solution was filtered and the solvent was removed *in vacuo*. The crude product was chromatographed on silica gel with a mobile phase of pentane and Et_2O (4:1). After the solvent was removed *in vacuo*, **1.17** was obtained as a yellow solid (101 mg, 85%). Crystals suitable for X-ray diffraction were grown from a saturated THF solution at –30 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 8.04 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.25-7.07 (m, 2H), 6.97 (t, *J* = 7.7 Hz, 1H), 6.90 (dd, *J* = 16.5, 6.3 Hz, 2H), 6.63 (d, *J* = 7.2 Hz, 1H), 5.29 (s, 1H), 4.27 (hept, *J* = 6.0 Hz, 1H), 3.47 (dt, *J* = 22.4, 9.1 Hz, 3H), 3.19 (dd, *J* = 14.8, 8.4 Hz, 2H), 3.08 (s, 1H), 2.77 (d, *J* = 10.1 Hz, 1H), 2.68 (dt, *J* = 13.7, 6.8 Hz, 1H), 2.25 (t, *J* = 17.8 Hz, 3H), 2.11 (s, 1H), 2.01 (dd, *J* = 21.0, 11.6 Hz, 2H), 1.70 (dd, *J* = 27.3, 8.9 Hz, 6H), 1.61 (d, *J* = 12.1 Hz, 1H), 1.52 (d, *J* = 14.6 Hz, 2H), 1.34 (s, 9H), 1.28-1.17 (m, 9H), 1.08 (dd, *J* = 12.9, 6.0 Hz, 6H), 0.91 (s, 9H). ^{13}C NMR (126 MHz, C_6D_6) δ 252.90, 218.88, 194.98, 194.47, 156.33, 149.54, 147.13, 136.66, 132.83, 132.57, 128.70, 126.07, 123.88, 123.83, 120.83, 113.30, 86.23, 70.06, 67.30, 63.12, 54.71, 45.57, 41.51, 40.69, 39.81, 39.37, 39.01, 37.63, 34.83, 32.95, 32.37, 31.15, 30.23, 29.98, 29.00, 28.69, 27.48, 27.00, 26.37, 26.29, 23.73, 22.99, 22.70, 22.61. HRMS (FAB+): Calculated – 814.3859, Found – 814.3871.



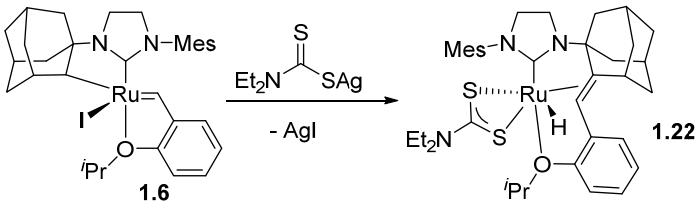
Synthesis of 1.18: In a glovebox, a Schlenk flask was charged with **1.5** (24 mg, 0.036 mmol) and *p*-benzoquinone (16 mg, 0.15 mmol). THF (2 mL) was added which resulted in an immediate color change from purple to red/orange. The flask was sealed, removed from the glovebox, and

heated to 70 °C for 12 h. After cooling to RT, the reaction was concentrated and the flask was taken back into the glovebox, where the red/brown residue was triturated with Et_2O to give **1.18** (6 mg, 13%) as a red crystalline solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.16 (t, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 2H), 6.92 (br s, 4H), 6.82 (t, *J* = 9.0 Hz, 4H), 6.77 (br s, 2H), 6.65 (s, 4H), 5.14 (s, 2H), 4.77 (dd, *J* = 7.5, 2.5 Hz, 2H), 4.58 (sept, *J* = 6.0 Hz, 2H), 4.19 (dd, *J* = 7.5, 2.5 Hz, 2H), 3.67 (quin, *J* = 9.5 Hz, 2H), 3.61 – 3.57 (m, 4H), 3.42 (t, *J* = 10.0 Hz, 2H), 3.19 (dd, *J* = 7.5, 3.0 Hz, 2H), 3.01 (br s, 2H), 2.83 (br d, *J* = 12.5 Hz, 2H), 2.43 (s, 6H), 2.16 (br d, *J* = 9.0 Hz, 2H), 2.1 – 2.08 (m, 2H), 2.06 (s, 6H), 1.93 (br s, 2H), 1.89 (s, 6H), 1.76 (br d, *J* = 11.5 Hz, 2H), 1.69 – 1.66 (m, 2H), 1.62 – 1.59 (m, 2H), 1.49 (br d, *J* = 11. 5 Hz, 2H), 1.40 – 1.38 (m, 2H), 1.35 – 1.32 (m, 2H), 1.22 (d, *J* = 6.0 Hz, 6H), 1.19 (d, *J* = 5.5 Hz, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 211.45, 163.30, 156.08, 150.53, 138.87, 137.96, 136.29, 135.59, 134.37, 129.98, 129.62, 129.45, 125.98, 119.24, 116.50, 113.50, 90.42, 88.63, 80.35, 77.04, 69.27, 65.11, 58.66, 46.11, 42.07, 41.30, 40.00, 38.66, 37.44, 31.97, 30.63, 29.30, 22.36, 22.27, 21.98, 19.42, 17.64. HRMS (FAB+): A mass corresponding to the monomeric species was detected. Calculated – 679.2474, Found – 679.2458.

Note: Class B alerts on the CIF file for compound **1.18** are due to the fact that the crystal is a twin with obvious edges for two components of stacked plates. It is not possible to account for this twinning in integration or refinement. Restraints were placed on the anisotropic placement parameters so as to approximate isotropic behavior. The crystal was obviously twinned but treated as a single component, therefore a negative peak of -4.7 e/A^3 and short C-C contact are a result. H1A and H1B are phenol protons, either one is an O-, changing the charge, or they accidentally refined too close together.

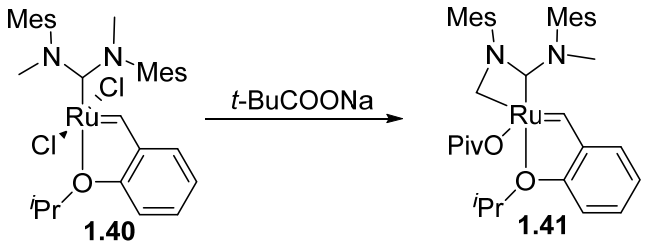


Synthesis of 1.20 and 1.21: In a glovebox, a Schlenk flask was charged with **1.19** (43 mg, 0.08 mmol), *t*-BuCOOAg (72 mg, 0.34 mmol) and THF (6 mL). The reaction was stirred at room temperature for 30 minutes. The solution was filtered through Celite and the solvent was removed *in vacuo* to yield crude **1.20**. After the solvent was removed *in vacuo*, crude **1.20** was taken up in DCM and layered with pentane. After sitting at room temperature overnight, the solvent was decanted and the remaining solid was washed with acetone and cold ether to yield **1.21** as a dark green solid (5.2 mg, 12%). Crystals suitable for X-ray diffraction were grown by a slow diffusion of pentane into a saturated benzene solution. ^{1}H NMR of **1.21** (500 MHz, CD_2Cl_2) δ 8.72 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.69 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.65 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.60-7.53 (m, 2H), 7.53-7.47 (m, 1H), 7.41-7.31 (m, 2H), 7.17-7.09 (m, 2H), 7.02 (td, *J* = 7.7, 0.9 Hz, 1H), 5.13 (sept, *J* = 6.1 Hz, 1H), 4.23 (br t 2H), 2.80 (s, 3H), 2.28 (s, 3H), 1.54 (br d, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 291.50, 222.37, 157.42, 142.86, 142.51, 139.54, 136.18, 136.01, 132.50, 130.58, 130.07, 128.45, 128.36, 126.88, 124.36, 121.14, 119.54, 117.57, 113.18, 75.16, 51.33, 23.97, 22.37, 19.26. HRMS (FAB+) of **1.20**: Calculated – 701.2529, Found – 701.2503. HRMS (FAB+) of **1.21**: Calculated – 568.0623 Found – 568.0610. NOTE: Further investigating of the ^{1}H NMR spectrum of **1.21** indicated the presence of a broad peak from 3.5-5.3 ppm that corresponds to two protons on the NHC backbone, at room temperature. Upon cooling to –20 °C however, we were able to see four distinct protons that corresponded to all four backbone protons on the NHC (Figures 34 and 35).



Synthesis of 1.22:

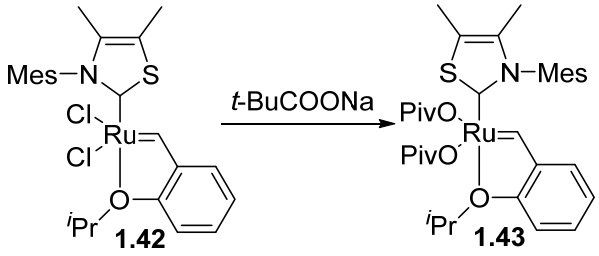
In a glovebox, complex **1.6** (52 mg, 0.075 mmol) was treated with silver (I) diethyldithiocarbamate (23 mg, 0.09 mmol) in THF (2.6 mL). The reaction was stirred at 35 °C for 1.5 h after which the solvent was removed *in vacuo*. The crude mixture was taken up in benzene and ran through a silica plug. A yellow band was isolated and provided product **1.22** (46 mg, 85% yield). ^{1}H NMR of **1.22** (500 MHz, C_6D_6) δ 7.59 (m, 2H), 8.87 (m, 2 H), 6.83 (s, 1H), 6.39 (m, 1H), 4.0 (sept., 1 H), 3.57 (m, 1H), 3.35 (m, 1H), 3.31 (m, 3H), 3.10 (d, 1 H), 2.87 (m, 3H), 2.78 (m, 1H), 2.57 (d, 1H), 2.39 (m, 6H), 2.33 (s, 1H), 2.25 (s, 1h), 2.18 (m, 1H), 2.87 (s, 3H), 2.12 (m, 1H), 2.05 (m, 2H), 1.90 (m, 1H), 1.80 (m, 3H), 1.70 (m, 1H), 1.50 (d, 3H). ^{13}C NMR (126 MHz, C_6D_6) δ 218.56, 211.15, 158.67, 139.22, 138.90, 137.36, 135.99, 135.72, 129.91, 128.95, 124.75, 120.82, 111.46, 77.87, 72.99, 61.71, 51.91, 49.59, 44.40, 42.88, 42.36, 41.27, 40.36, 39.57, 38.80, 35.70, 34.14, 31.22, 30.72, 23.61, 21.28, 20.46, 19.76, 19.49, 13.19, 12.74. HRMS (FAB+) of **1.22**: Calculated – 718.2439, Found – 718.2466.



Synthesis of 1.41:

In a glovebox, complex **1.40** (50 mg, 0.08 mmol) was treated with *t*-BuCOONa (99 mg, 0.80 mmol) in a 1:1 THF/MeOH mixture (5 mL). The reaction was stirred at 35 °C for 1 h after which

the solvent was removed *in vacuo*. Pentane was added and the crude was filtered over Celite to remove sodium salts. The pentane solution was placed into freezer and blue crystals had crashed out after sitting overnight. The crystals were dissolved in a 4:1 mixture of pentane and diethyl ether and run through a silica plug. A blue band was isolated and the solvent was removed *in vacuo*, providing **1.41** (18 mg, 34% yield).



Synthesis of 1.43:

In a glovebox, complex **1.42** (50 mg, 0.097 mmol) was treated with *t*-BuCOONa (120 mg, 0.97 mmol) in a 1:1 THF/MeOH mixture (4 mL). After stirring at RT for 3 h, the solvent was removed *in vacuo*. The crude mixture was taken up in DCM and filtered through Celite to remove sodium salts and the solvent was removed *in vacuo*. The resulting solid was taken up in a mixture of diethyl ether and pentane and placed in the freezer. Green crystals had formed after letting the mixture sit overnight, providing complex **1.43** (28 mg, 42% yield).

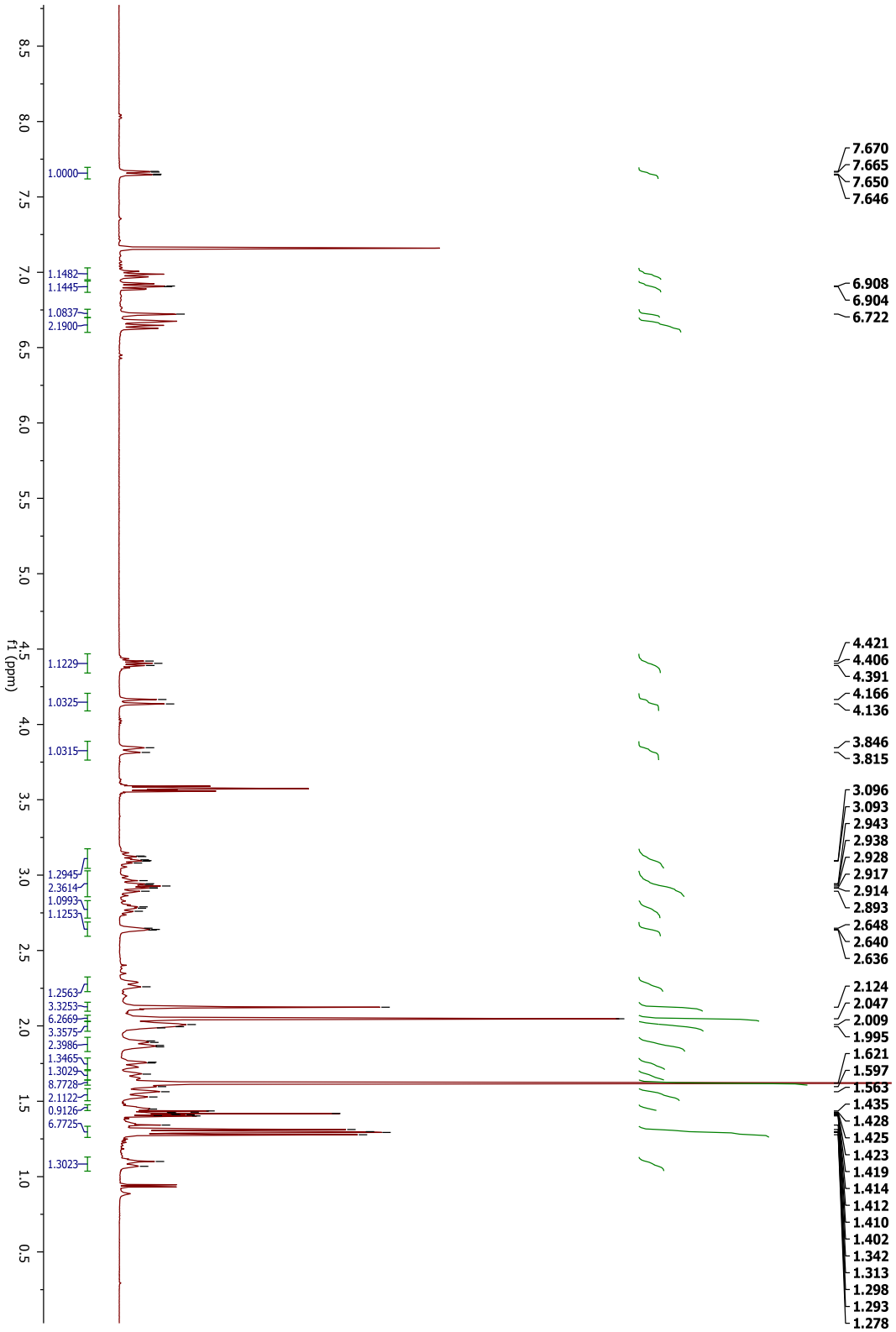


Figure 18. ^{1}H NMR (400 MHz) spectrum of **1.15** in C_6D_6.

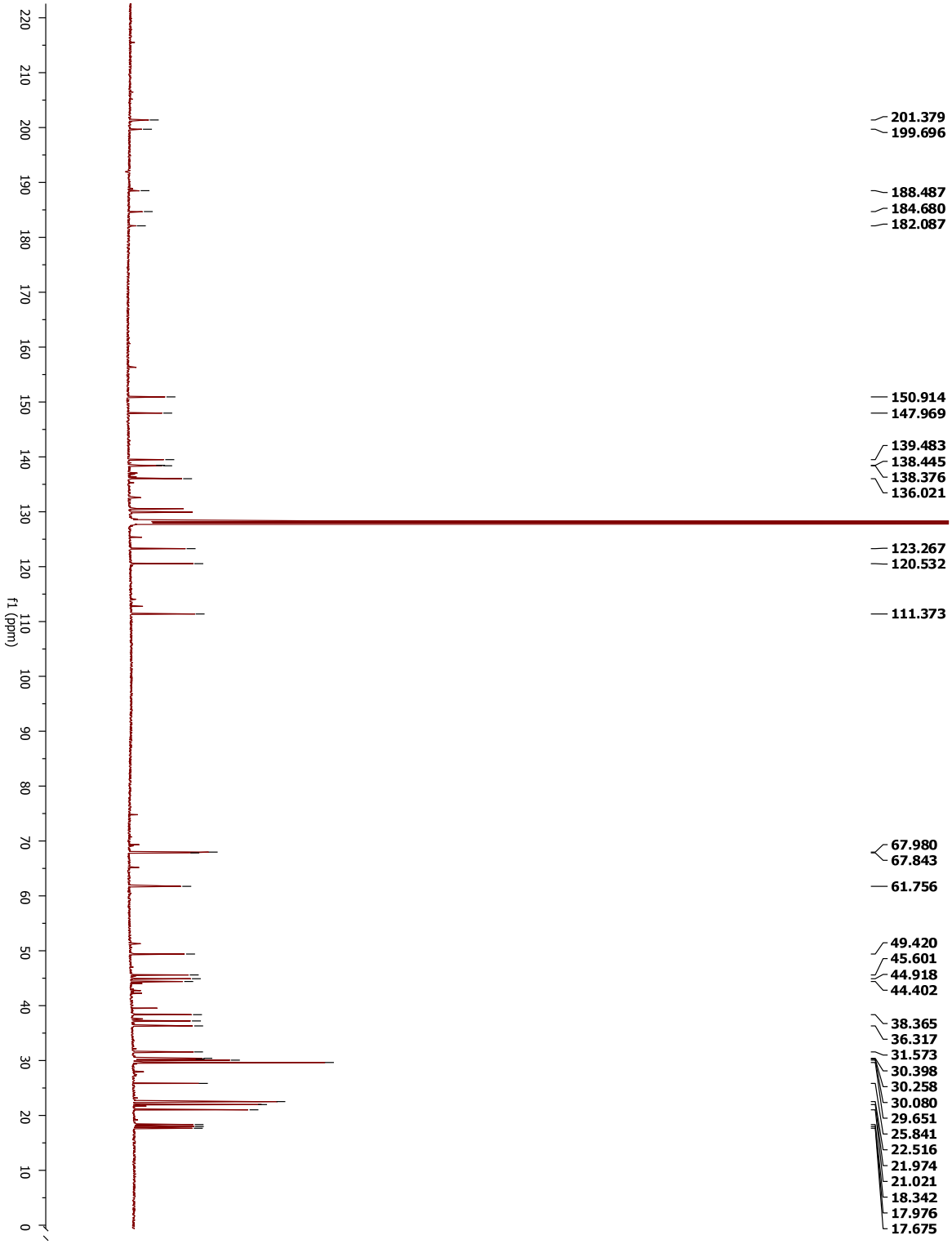


Figure 19. ^{13}C NMR (101 MHz) spectrum of **1.15** in C_6D_6.

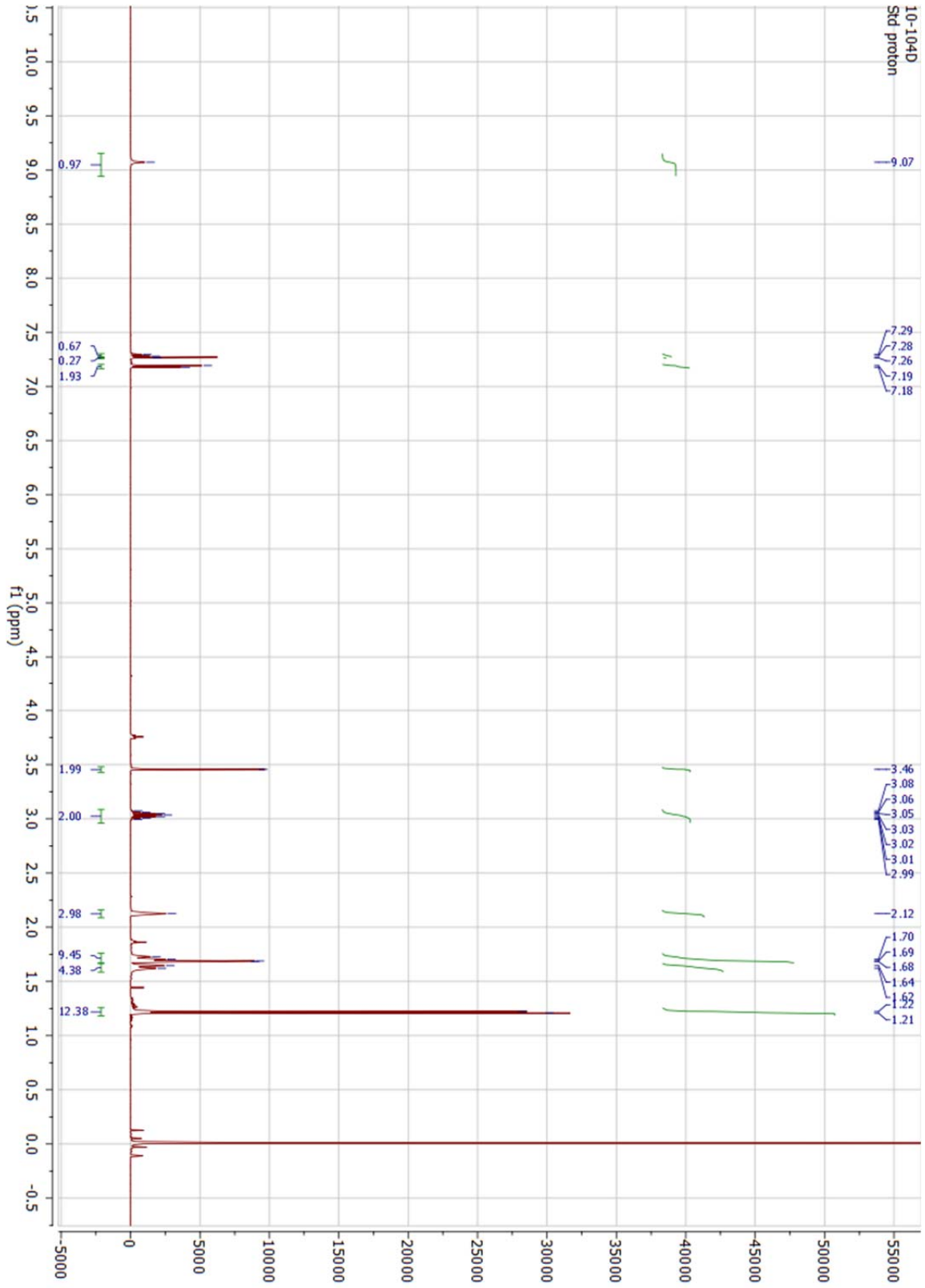


Figure 20. ^{1}H NMR (500 MHz) spectrum of **1.47** in $CDCl_3$.

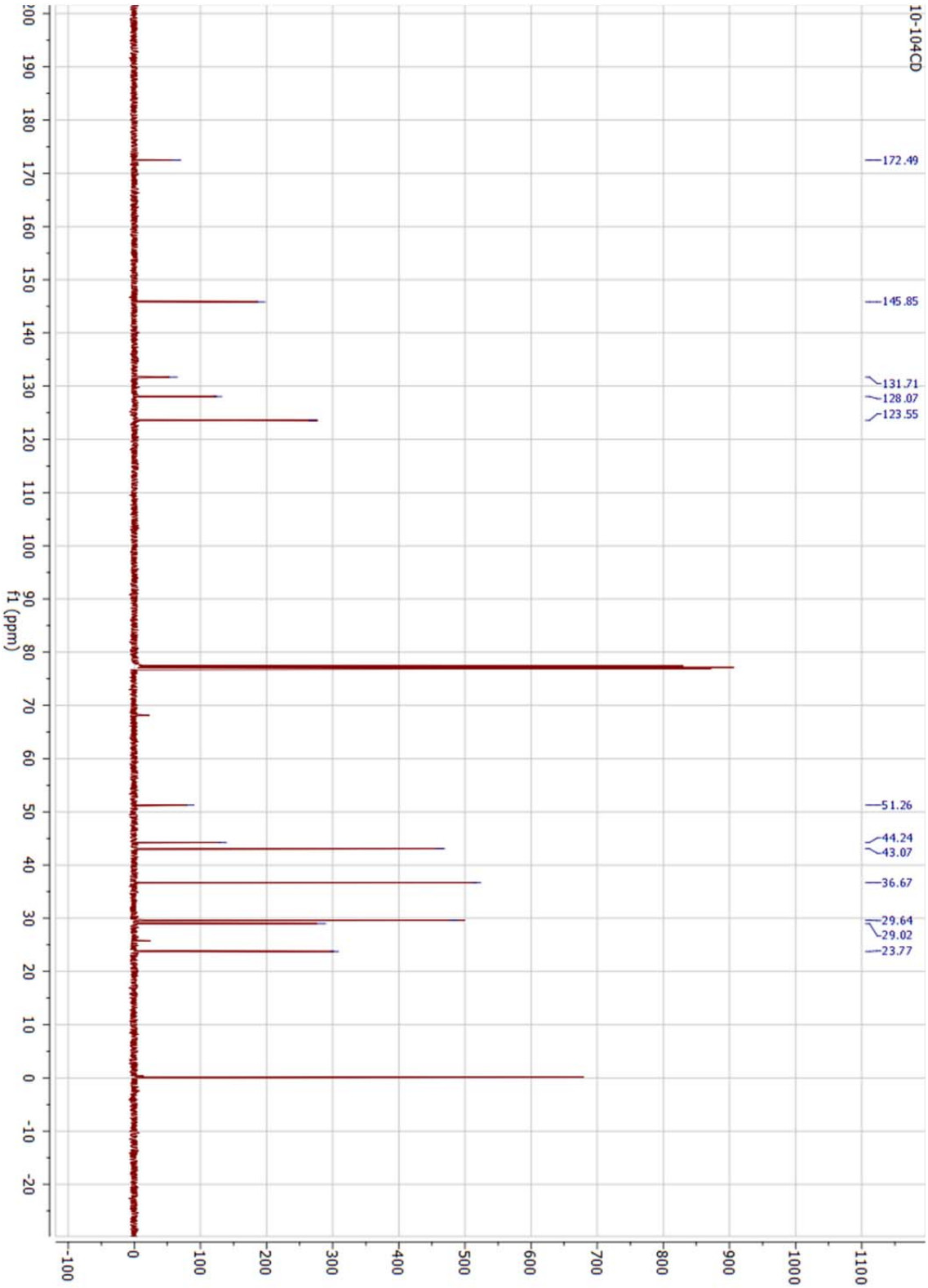


Figure 21. ^{13}C NMR (126 MHz) spectrum of **1.47** in $CDCl_3$.

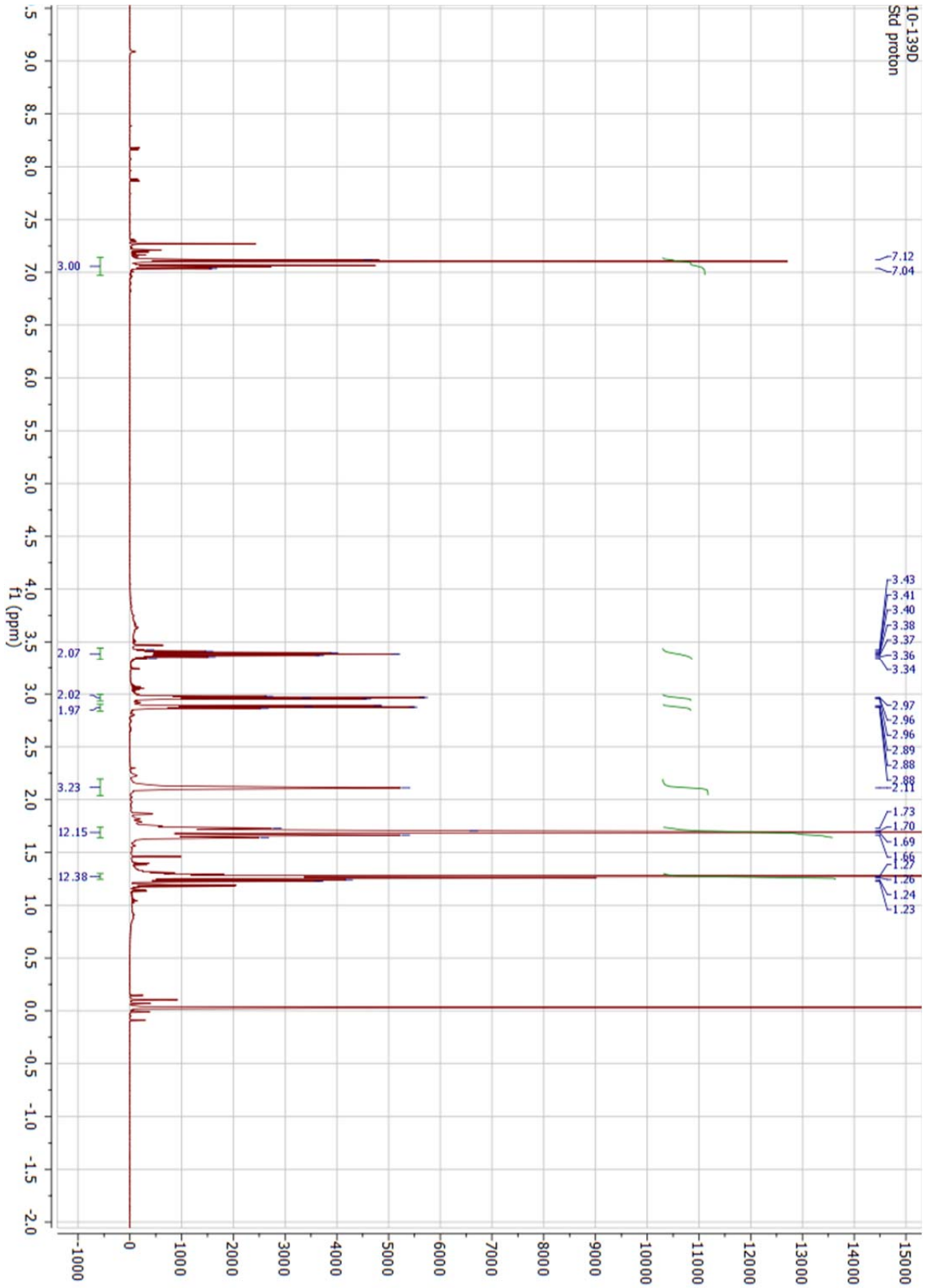


Figure 22. ^{1}H NMR (500 MHz) spectrum of **1.48** in $CDCl_3$.

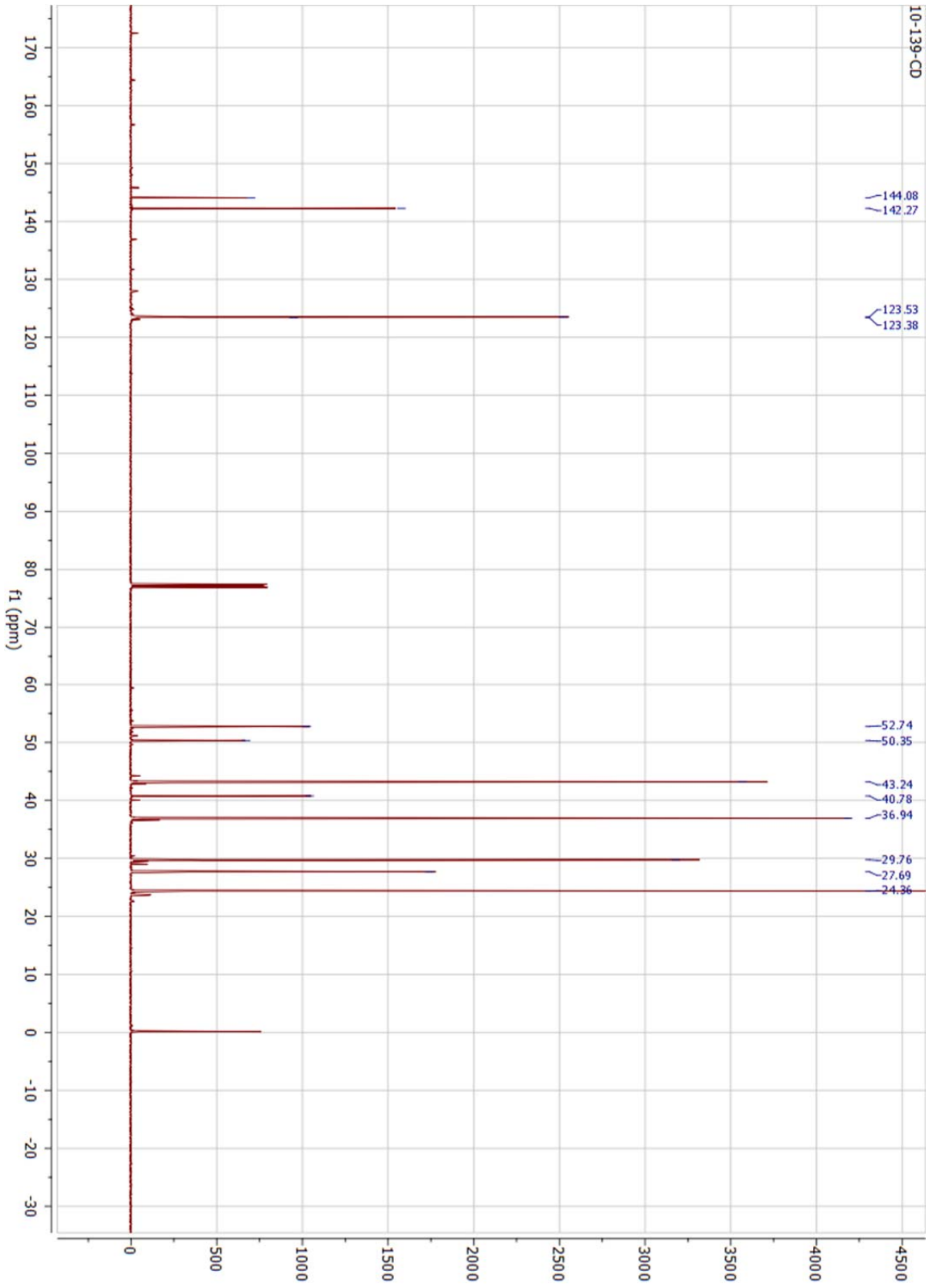


Figure 23. ^{13}C NMR (126 MHz) spectrum of **1.48** in $CDCl_3$.

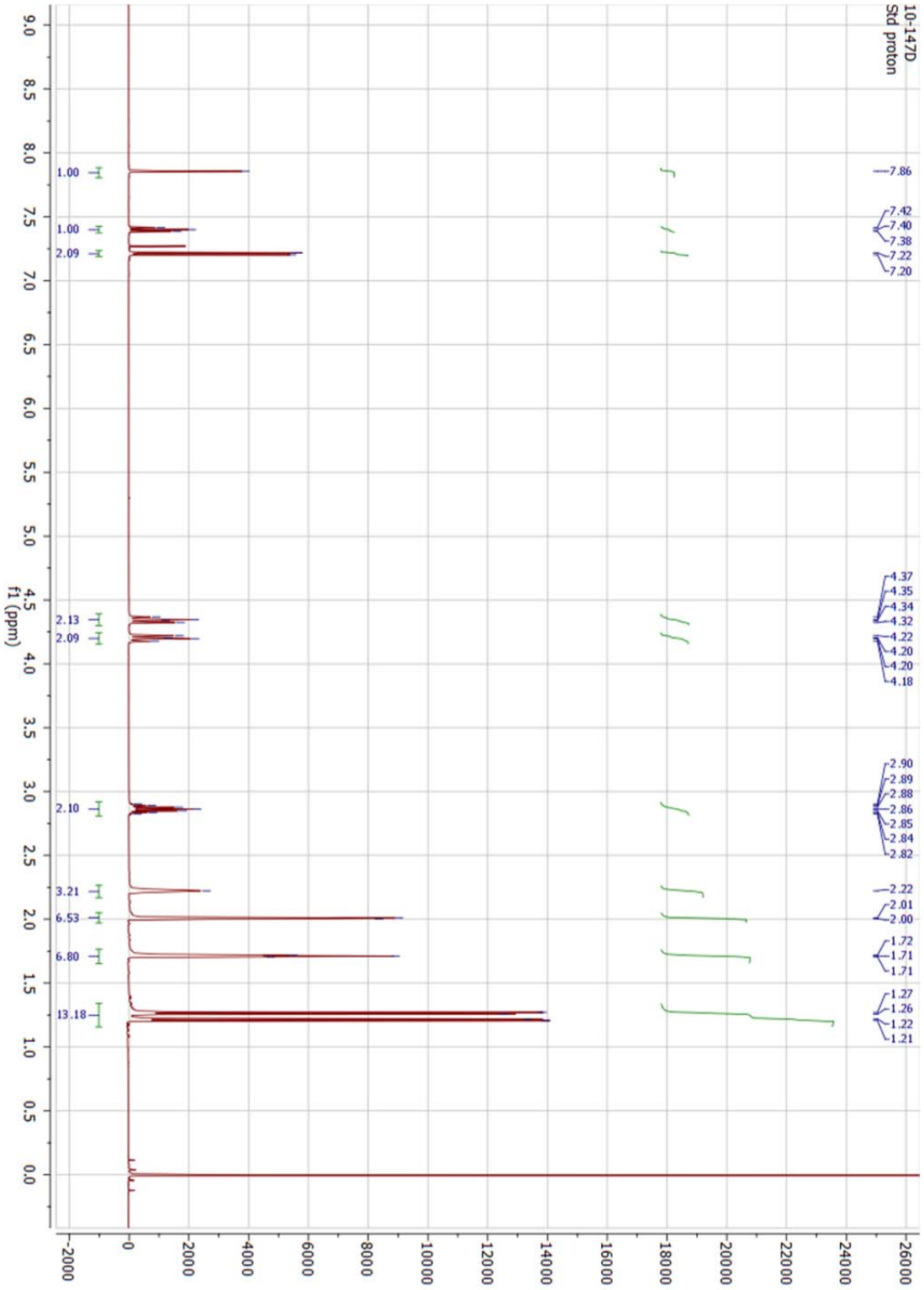


Figure 24. ^{1}H NMR (500 MHz) spectrum of **1.49** in $CDCl_3$.

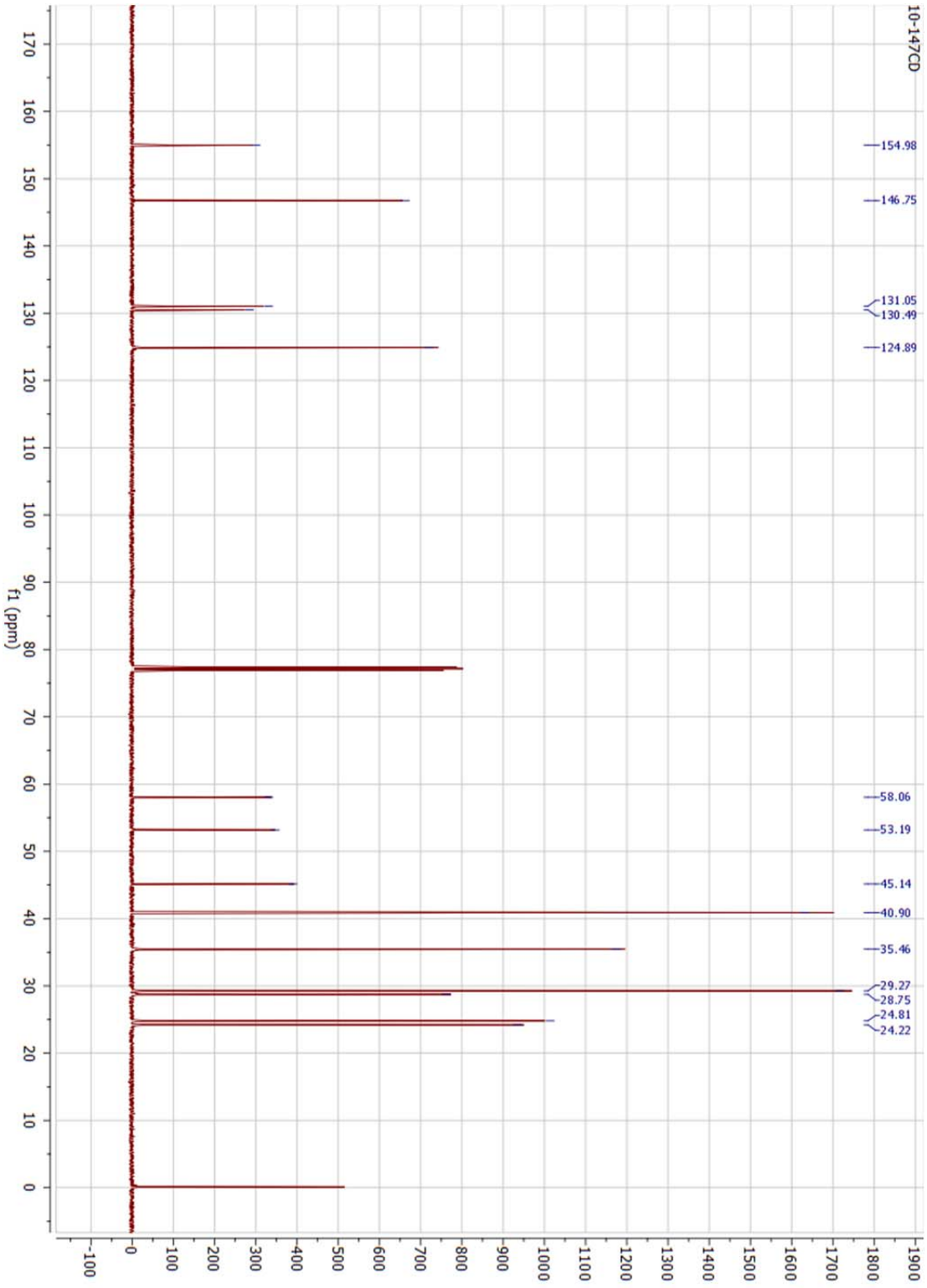


Figure 25. ^{13}C NMR (126 MHz) spectrum of **1.49** in $CDCl_3$.

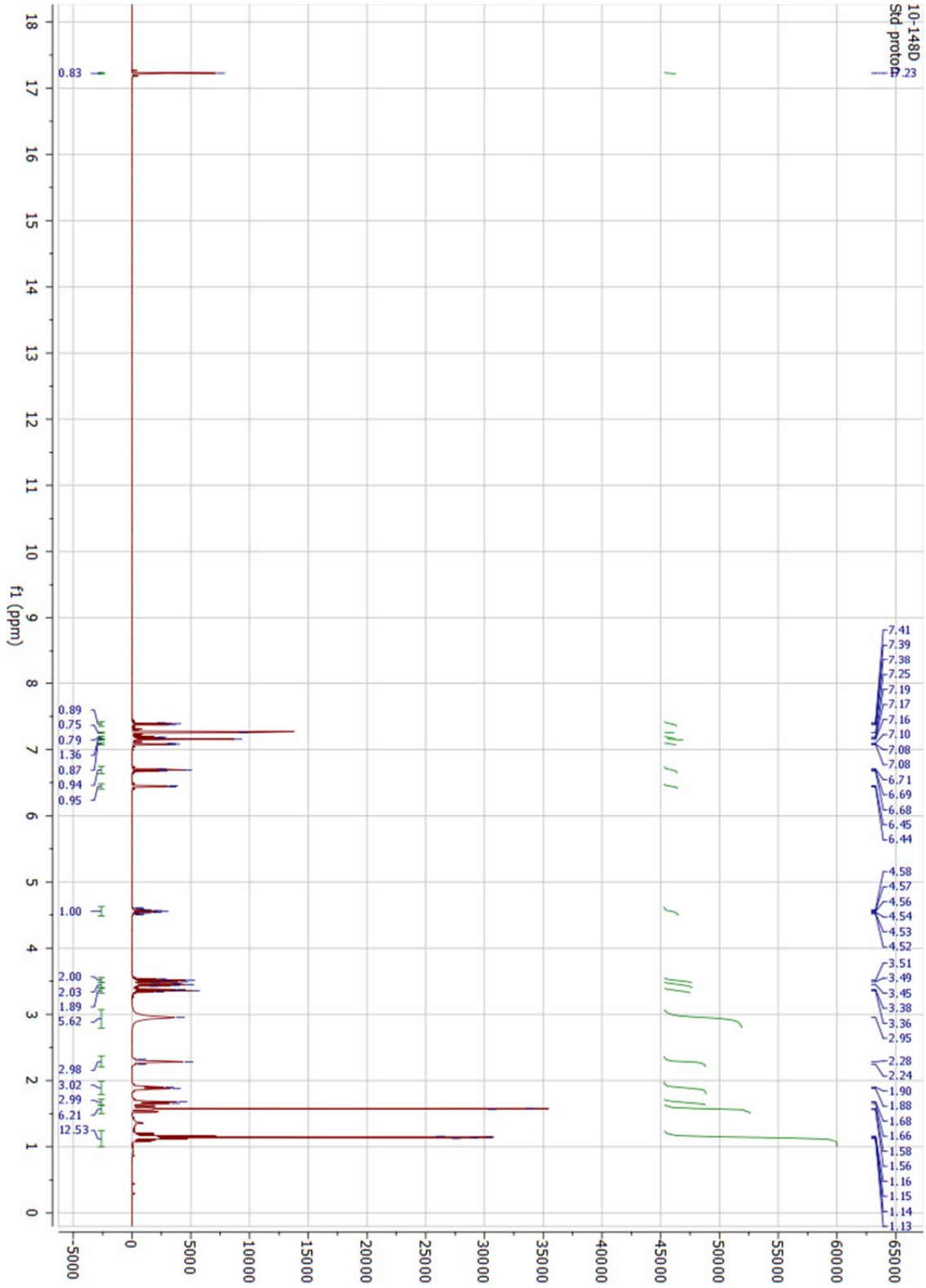


Figure 26. ^{1}H NMR (500 MHz) spectrum of **1.16** in C_6D_6.

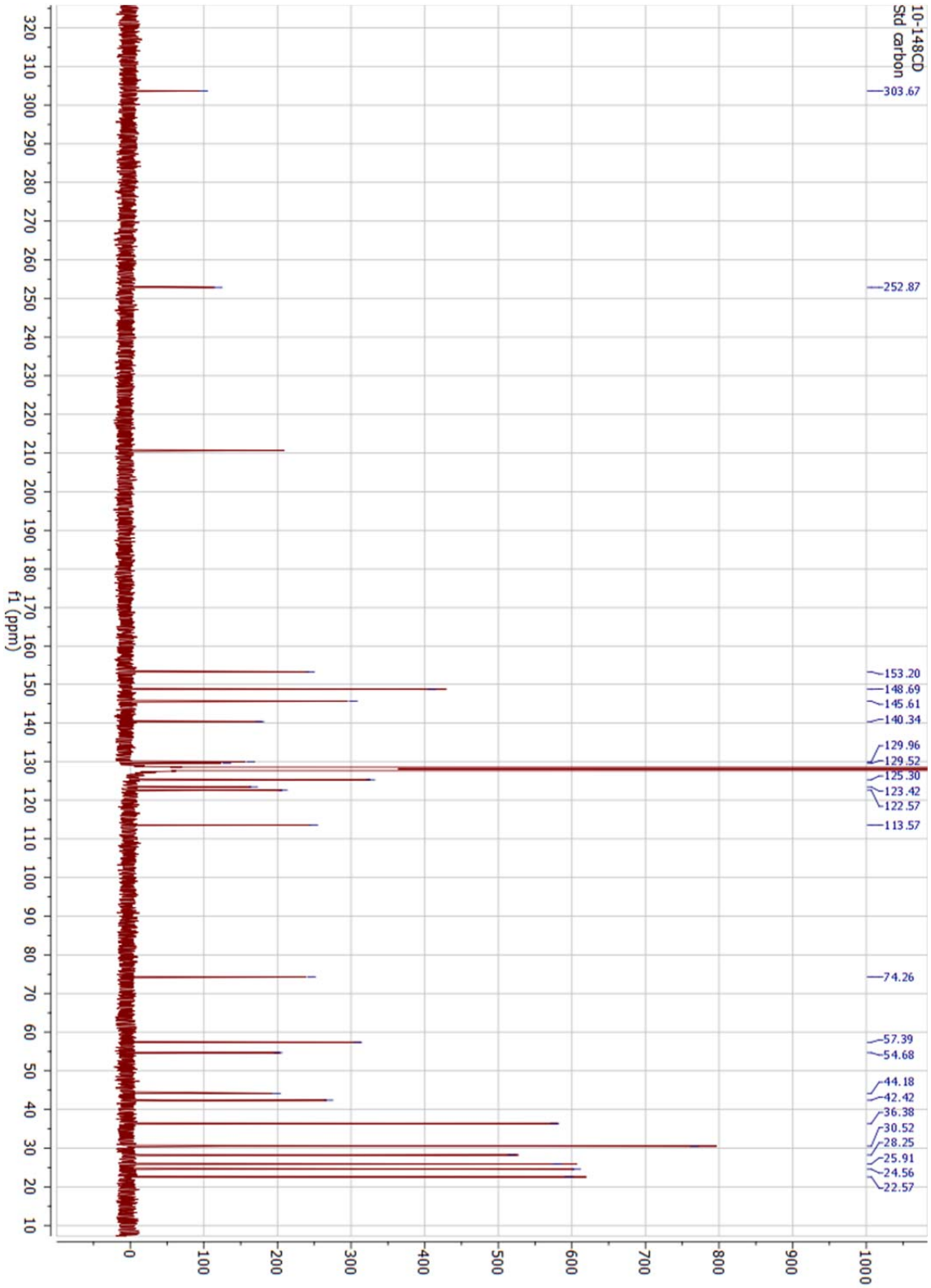


Figure 27. ^{13}C NMR (126 MHz) spectrum of **1.16** in C_6D_6.

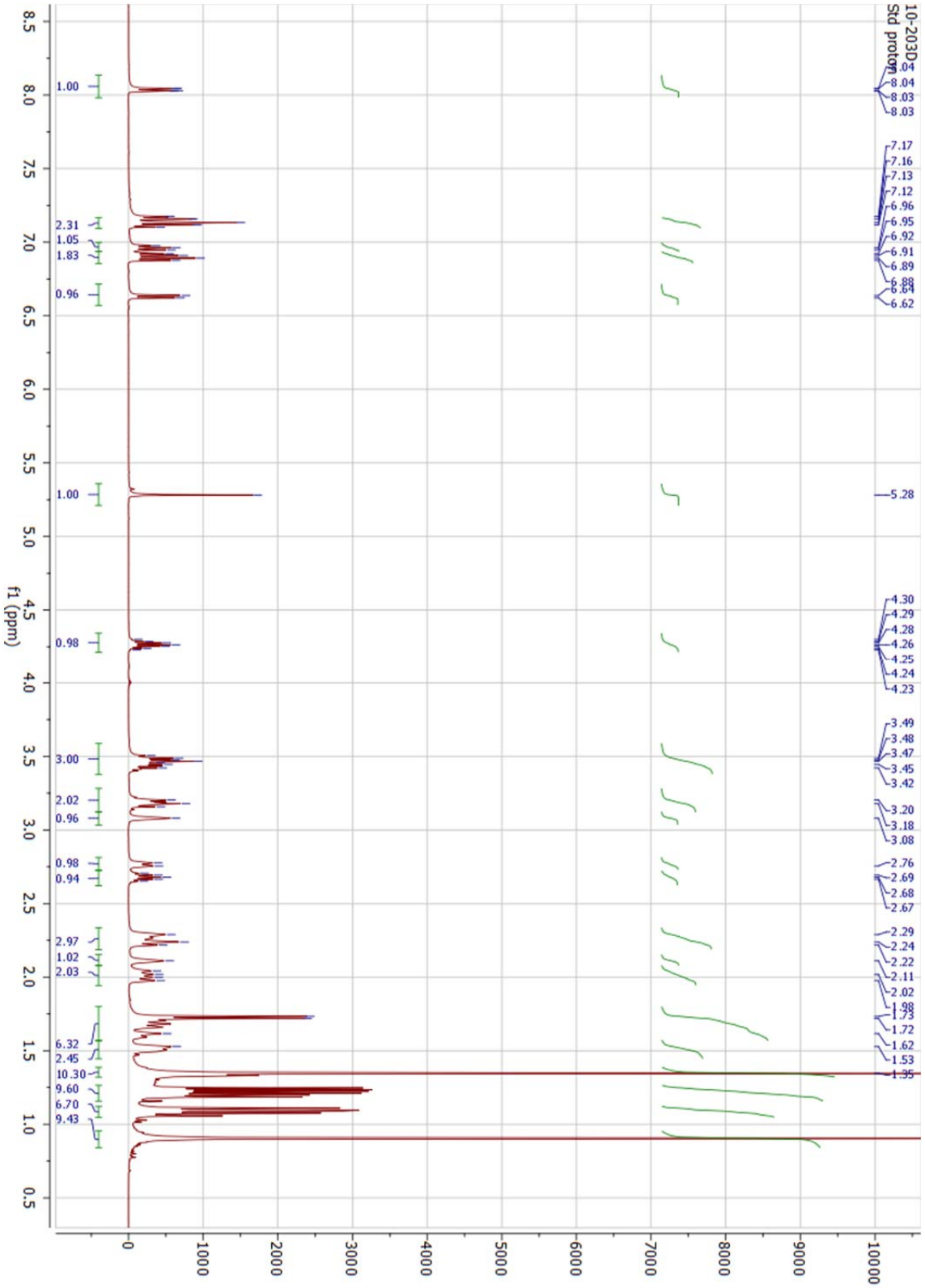


Figure 28. ^{1}H NMR (500 MHz) spectrum of **1.17** in C_6D_6.

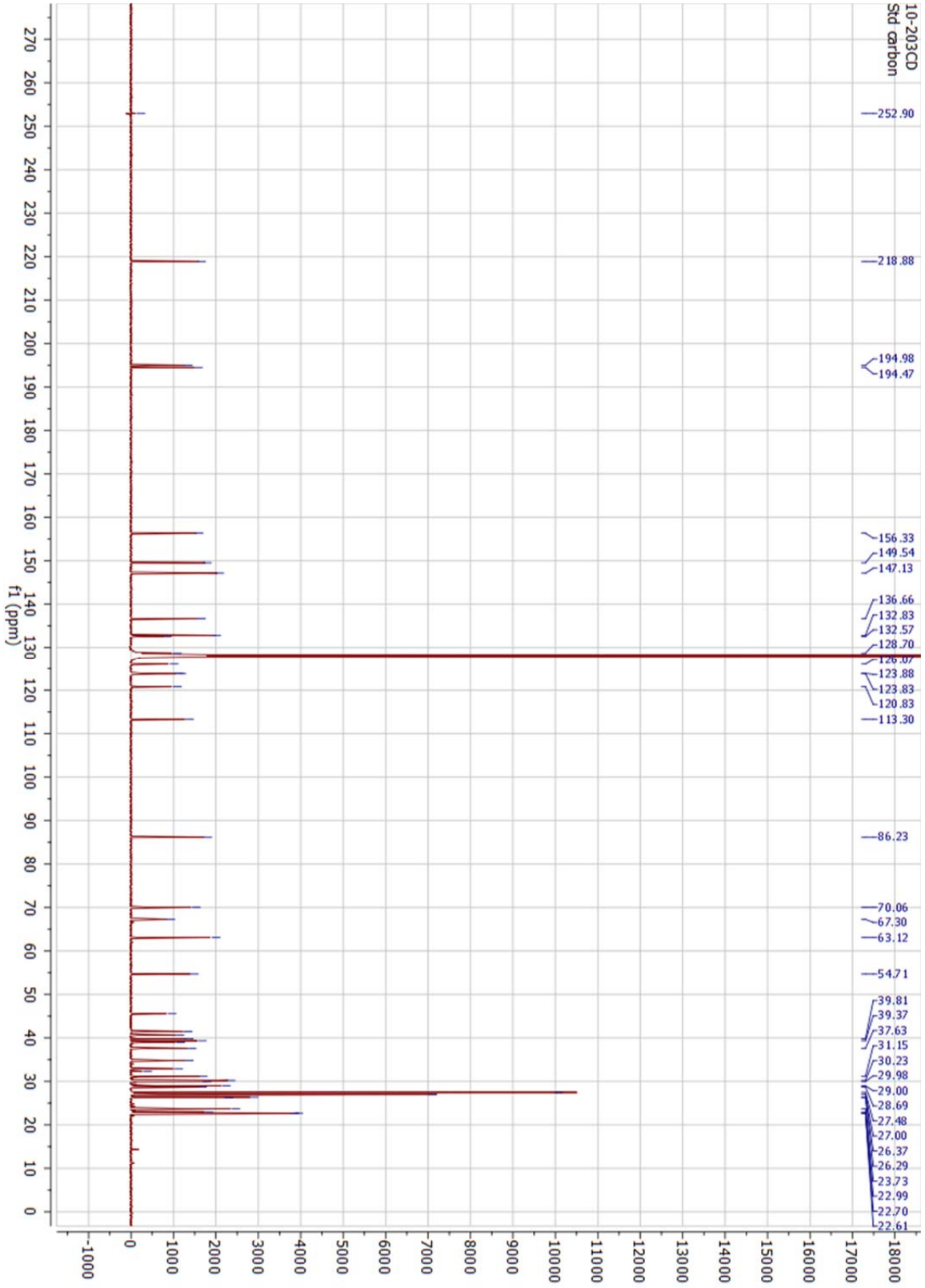


Figure 29. ^{13}C NMR (126 MHz) spectrum of **1.17** in C_6D_6.

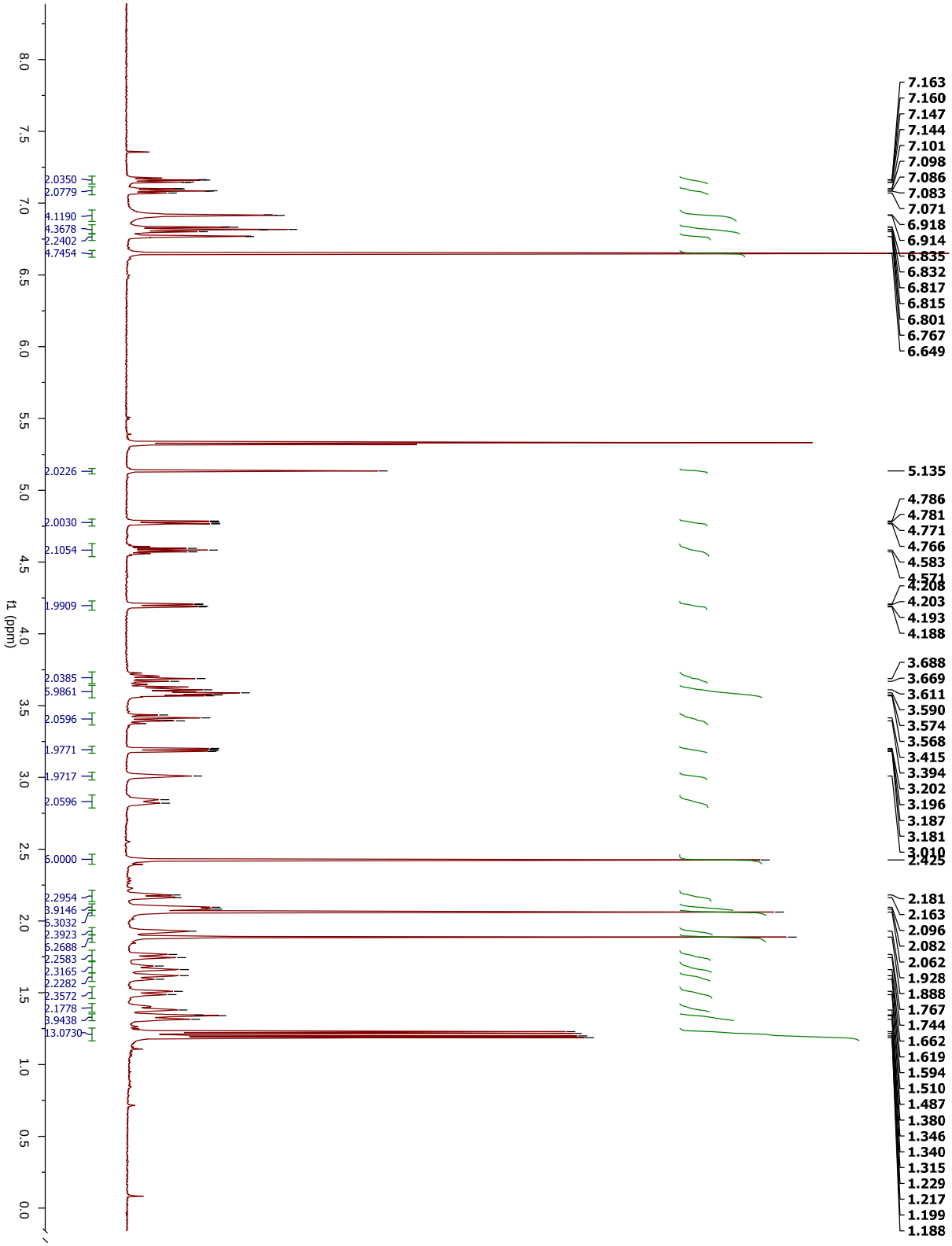


Figure 30. ^{1}H NMR (500 MHz) spectrum of **1.18** in CD_2Cl_2.

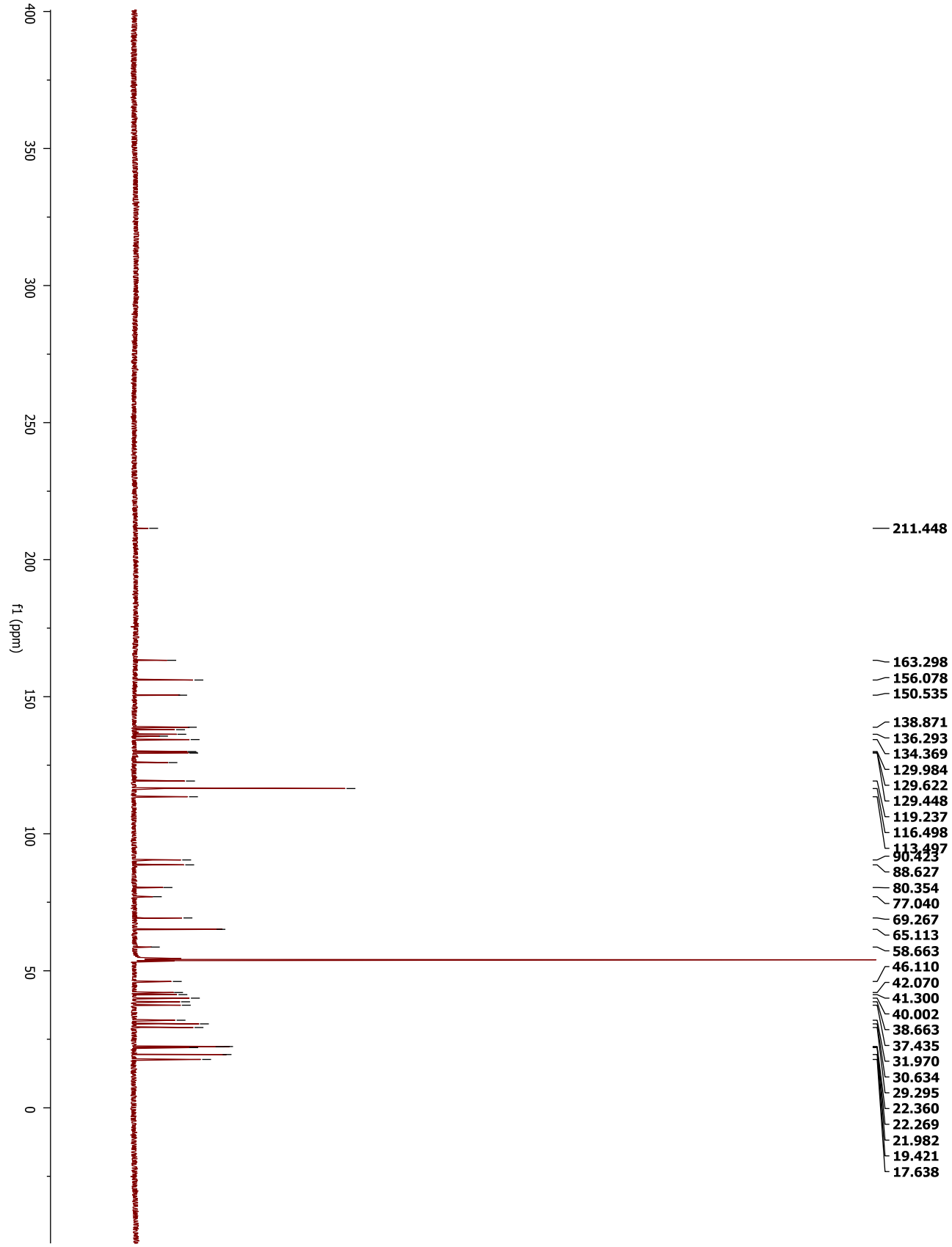


Figure 31. ^{13}C NMR (126 MHz) spectrum of **1.18** in CD_2Cl_2**.**

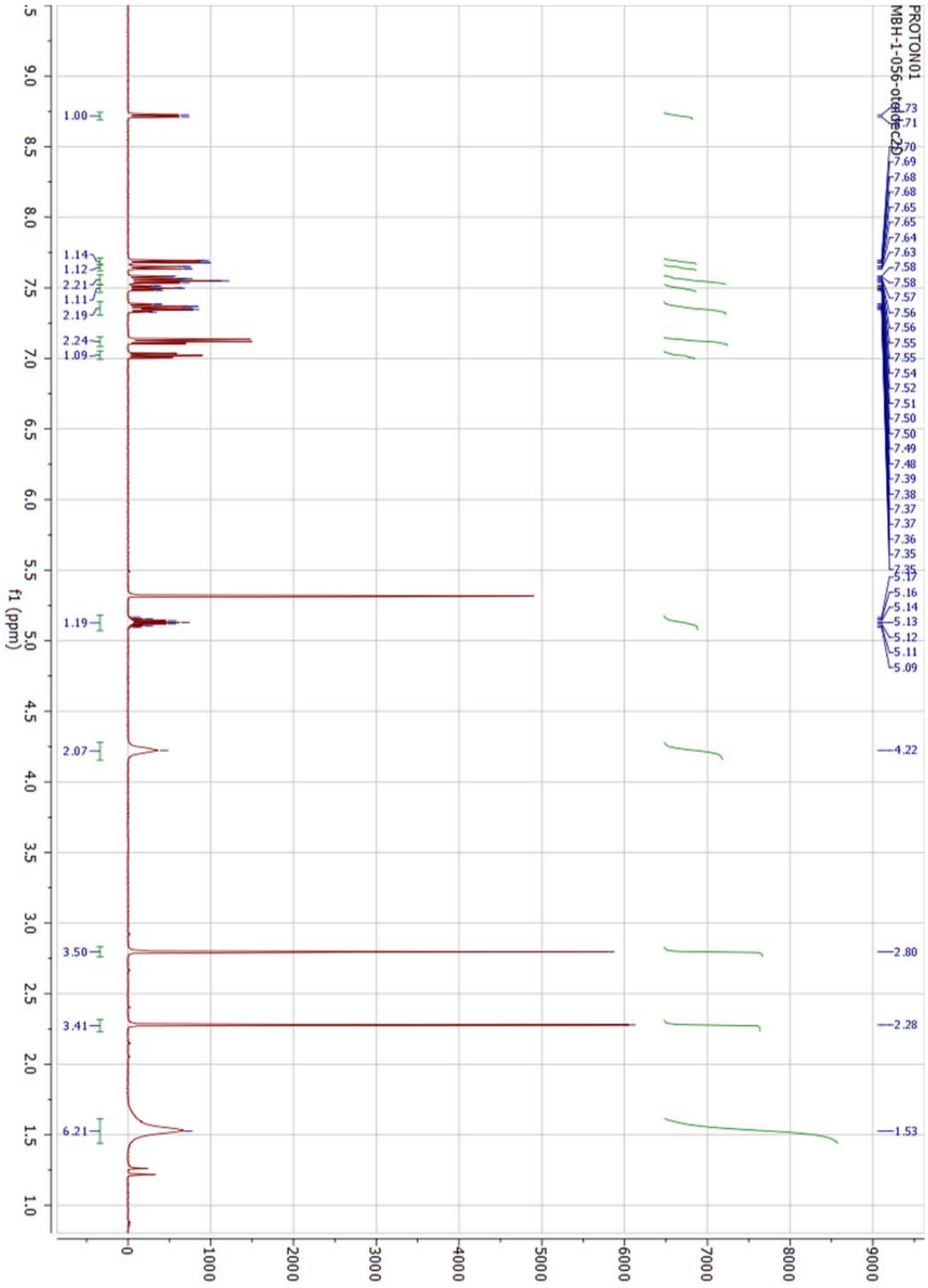


Figure 32. ^{1}H NMR (500 MHz) spectrum of **1.21** in CD_2Cl_2.

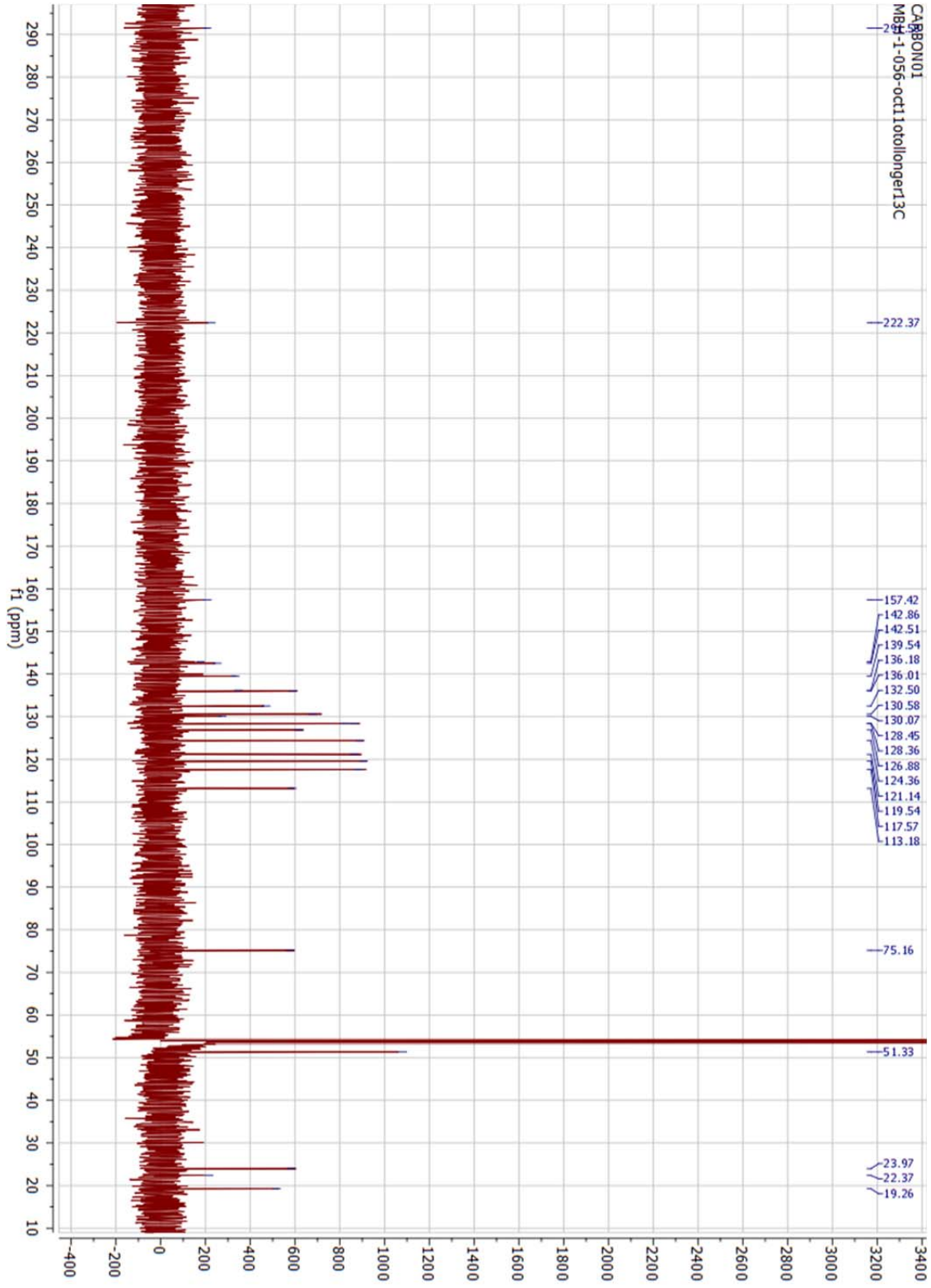


Figure 33. ^{13}C NMR (126 MHz) spectrum of **1.21** in CD_2Cl_2.

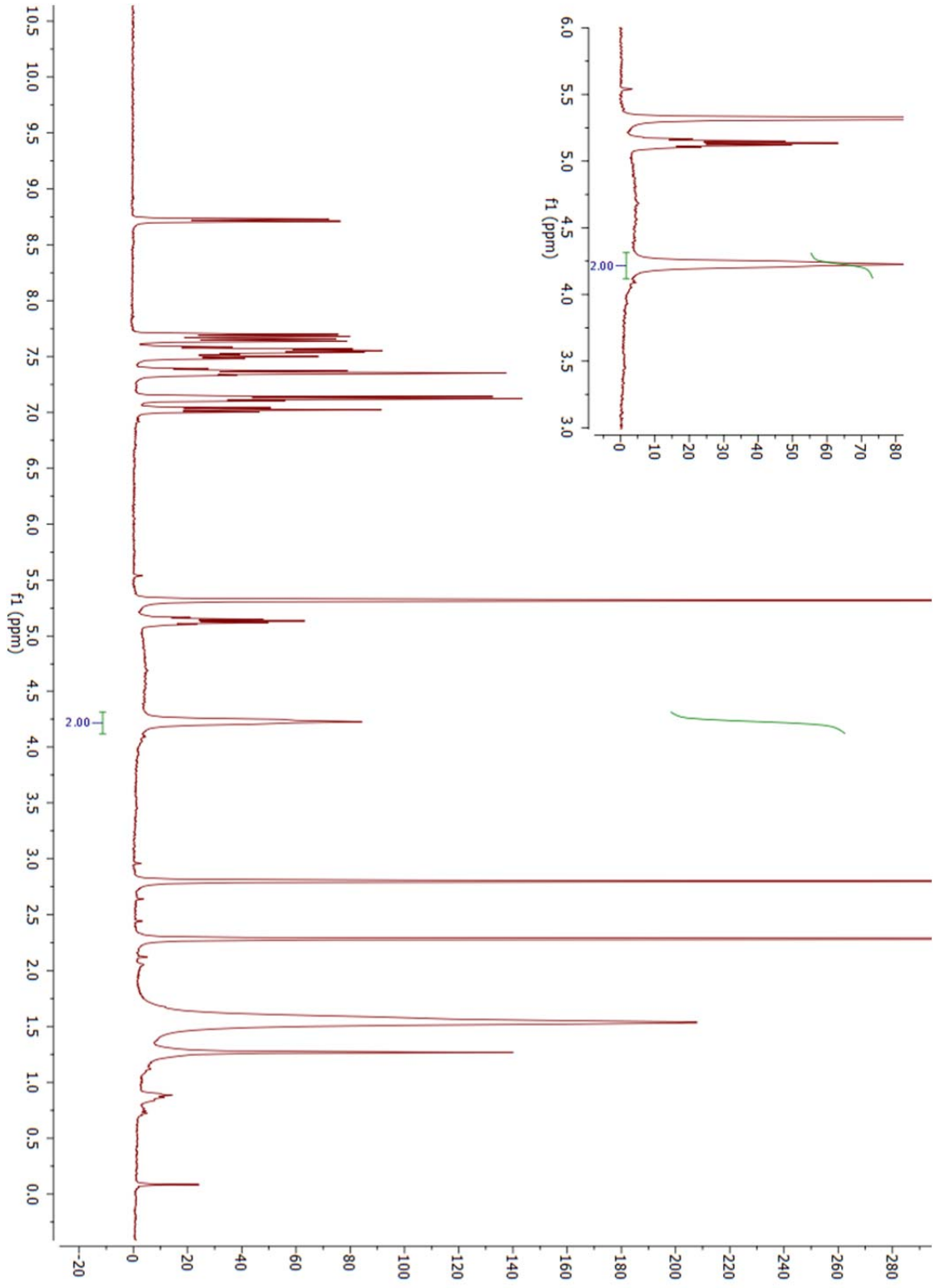


Figure 34. ^{1}H NMR (400 MHz) spectrum of **1.21** in CD_2Cl_2 at 25 °C**.**

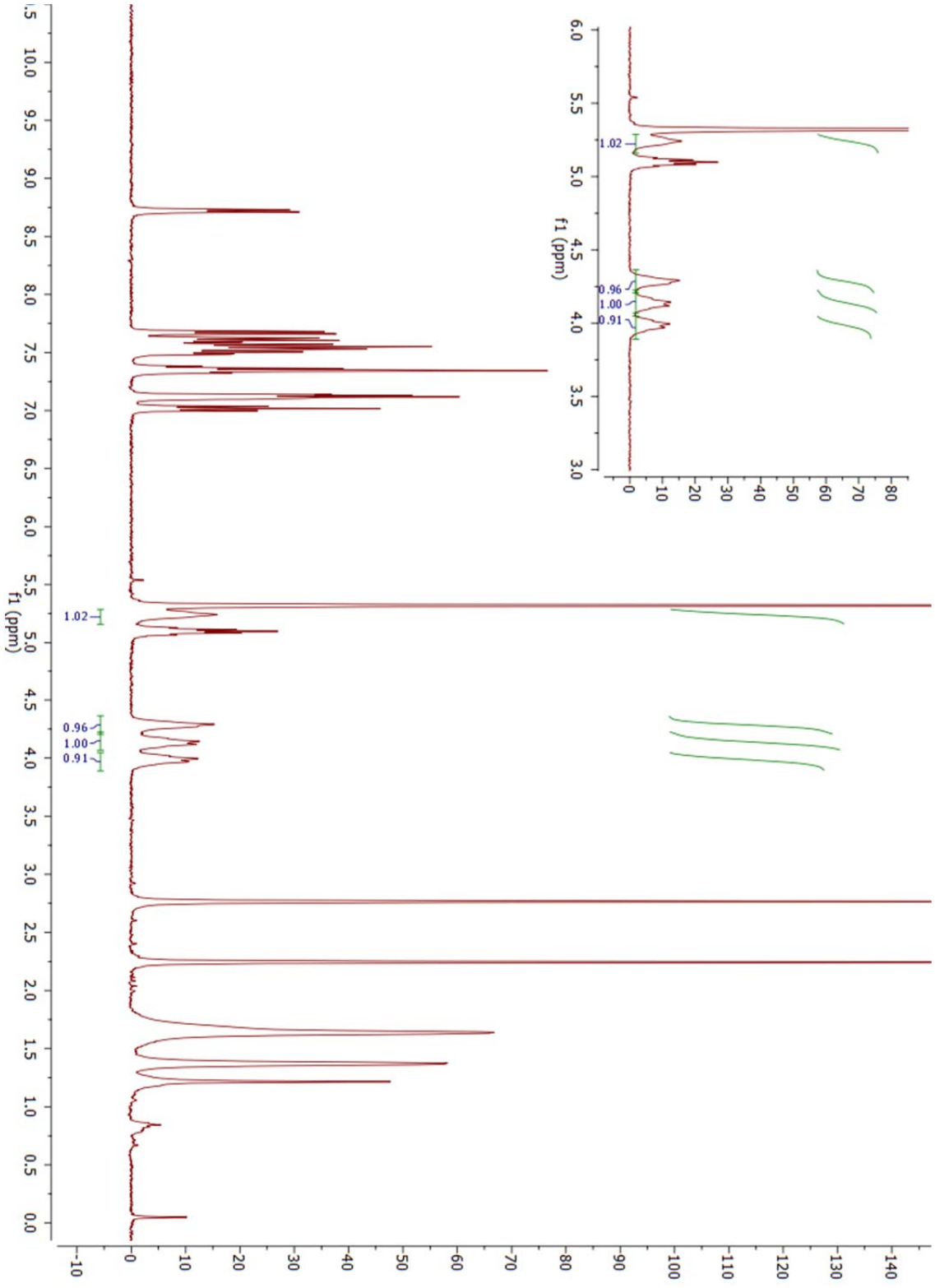


Figure 35. ^{1}H NMR (400 MHz) spectrum of **1.21** in CD_2Cl_2 at –20 °C.

C h a p t e r 2

SYNTHETIC APPLICATIONS OF HIGHLY *Z*-SELECTIVE RUTHENIUM METATHESIS CATALYSTS

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Herbert, M. B.; Marx, V. M.; Pederson, R. L.; Grubbs, R. H. *Angew. Chem. Int. Ed*. **2013**, *52*, 310.

Miyazaki, H.; Herbert, M. B.; Liu, P.; Dong, X.; Xu, X.; Keitz, B. K.; Ung, T.; Mkrtumyan G.; Houk, K. N.; Grubbs, R. H. *J. Am. Chem. Soc.* **2013**, *135*, 5848.

Marx, V. M.; Herbert, M. B.; Keitz, B. K.; Grubbs, R. H. *J. Am. Chem. Soc*. **2013**, *135*, 94.

ABSTRACT:

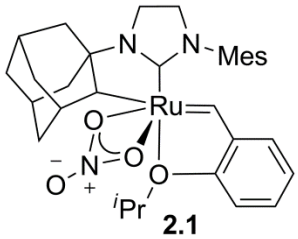
After the discovery and development of highly active and *Z*-selective NHC-chelated ruthenium alkylidene complexes (Chapter 1), these species were evaluated as catalysts for the formation of natural and unnatural products bearing or derived from *Z*-olefins. In particular, Lepidopteran insect female sex pheromones were synthesized using *Z*-selective cross metathesis. Such species are commonly used as green and non-toxic pesticide alternatives in pest control applications. Macrocyclic musk fragrances were also formed in a facile manner using *Z*-selective macrocyclic ring closing metathesis; certain musk fragrances are comprised of macrocycles and are generally isolated in small quantities from plants and animals. As a complementary approach to the formation of highly *Z*-products, the selective degradation of *Z*-olefins using *Z*-selective ethenolysis was investigated using our family of chelated catalysts. It was shown that in stereoisomeric mixtures of *E*- and *Z*-olefins, the *Z*-isomer can selectively be ethenolyzed providing purely *E*-olefins bearing various functional groups.

SYNTHESIS OF LEPIDOPTERAN INSECT PHEROMONE CROSS PRODUCTS:

The use of insect sex pheromones to limit specifically targeted pest populations has gained increasing popularity as a viable, safe, and environmentally-friendly alternative to insecticides. While broad spectrum insecticides are toxic compounds that have been shown to adversely affect human health,[1] extensive studies have revealed that insect pheromones are nontoxic and safe for human consumption at the levels used in pest control practices.[2] Female sex pheromones are mainly employed in pest control in a process termed mating disruption. This involves dispersing pheromones over a large area of crops, overloading the sensory organs of male insects and preventing them from locating and mating with females who are releasing a

much smaller amount of the same pheromone blends; this strategy has proven to reduce specific insect populations dramatically.[3] Pheromones also play an essential role in integrated pest management (IPM), which involves monitoring insect populations in a particular area. The amount of insects captured in traps releasing pheromones is correlated to the population of the pest; this allows for a more targeted and less wasteful approach to pest control. To date, the United States Environmental Protection Agency (EPA) has approved approximately twenty lepidopteran female sex pheromones as active ingredients for pest control.[2]

The lepidopteran order of insects includes extensive families of butterflies and moths whose larvae can devastate critical and valuable crops; it is estimated that insects destroy approximately 13% of food crops in the United States each year. The majority of known lepidopteran sex pheromones are straight-chained hydrocarbon acetates, alcohols, and aldehydes containing one to three double bonds with various olefin geometries. The facile formation of *E*-olefin containing pheromones using olefin metathesis has been reported, however the efficient synthesis of *Z*-containing pheromones has remained a challenge.[4] Current routes to such species involve wasteful processes including the Lindlar hydrogenation of alkynes and the Wittig reactions, among others.[5] Due to difficulty in completely removing the palladium hydrogenation catalyst and the high toxicity of the lead reagent necessary to prevent over-reduction, the Lindlar hydrogenation of alkynes is not an optimal route to *Z*-olefins. Similarly, the Wittig reaction is not ideal due to the use of stoichiometric reagents and difficulty removing phosphine oxide byproducts. Key advantages of using olefin metathesis are that reactions can be run at ambient temperatures with starting materials derived from commodity materials like α-olefins and seed oils.



2.1

Figure 1: Previously reported chelated catalyst for *Z*-selective olefin metathesis.

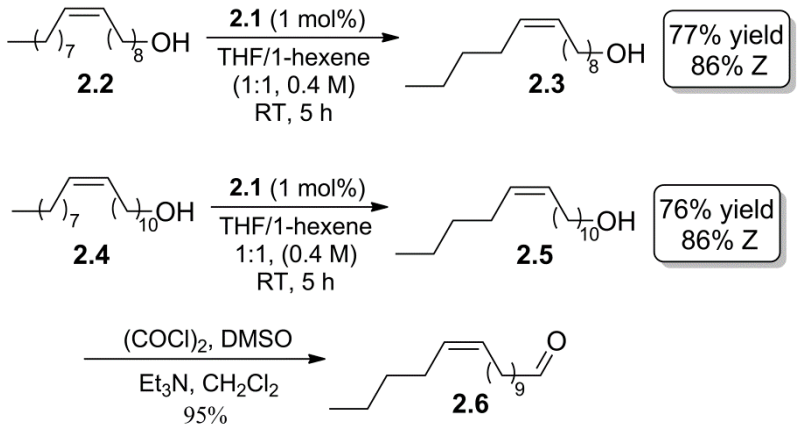
As previously mentioned, we have developed a family of functional-group tolerant, ruthenium-based *Z*-selective metathesis catalysts and, using optimized nitrato-type catalyst **2.1**, a monounsaturated *cis*-olefin containing pheromone was synthesized (Figure 1). Catalyst **2.1** has been shown to be an improvement over previously reported carboxylate-substituted catalysts in terms of activity, stability, and *Z*-selectivity.[6] The elucidation of methods to form pheromones containing stereopure *E*- and *Z*-olefins is of high importance because even minute amounts of stereoisomeric impurities can cause undesired effects in pest control applications. We desired to demonstrate the efficacy of **2.1** by synthesizing a set of *cis* insect pheromones with diverse functionality while simultaneously investigating the reactivity of catalyst **2.1** in more complicated cross metathesis reactions.

Nine lepidopteran female sex pheromones currently approved by the EPA as insecticide alternatives were chosen as synthetic targets, and it was surmised that the chosen compounds could be formed at ambient temperatures from renewable and commercially-available chemicals with a minimal amount of steps and low catalyst loadings of **2.1**.[7] Alcohol-substituted species were chosen as substrates because simple manipulations, such as acetylation or oxidation, could be subsequently carried out to produce the desired pheromones. It is envisioned that the methods developed could be elaborated to rapidly synthesize other well-studied insect pheromones containing *cis*-olefins not yet approved by the EPA for pest control.

The metathesis of seed oils offers new synthetic routes to high value products from renewable resources with high chemoselectivity.[8] Currently, plant oils are the most important renewable raw

material for the chemical industry and products derived from them are used heavily as surfactants, cosmetic products, and lubricants. Moreover, the use of seed oil-based feedstocks in environmentally benign and sustainable chemical manufacturing has the potential to greatly reduce net CO_2 emissions.[9] Convenient for our purposes, the large-scale production of fatty acid methyl esters has increased dramatically during the last ten years because of the industrial utilization of biodiesel.[10] We suspected that a number of the pheromone targets could be synthesized by the *Z*-selective cross metathesis of various terminal olefins with the seed oil derivatives oleyl alcohol (**2.2**) and 11-eicosenol (**2.4**). These long chain primary alcohols contain one 1,2-disubstituted *cis*-double bond and are obtained by the transesterification and reduction of a number of seed oils, including canola and jojoba oil. Since oleyl alcohol and 11-eicosenol are obtained by the reduction of analogous esters, we surmised that using such alcohol-containing starting materials would provide a facile, cheap, and renewable route to high value insect pheromones.

It was discovered that 1-hexene could be reacted with the aforementioned seed oil derivatives in the presence of catalyst **2.1** (1 mol %) to yield the desired cross products in good yields with high *cis*-selectivity (Scheme 1). The reaction of 1-hexene with oleyl alcohol directly produced **2.3** in 77% yield and with 86% of the *Z*-olefin isomer. The corresponding product (**2.5**) derived from 11-eicosenol was obtained in 75% yield and with 86% *Z*-olefin, and was subsequently oxidized under Swern conditions to yield pheromone **2.6**; the syntheses reported here are the shortest routes to form pheromones **2.3** and **2.6**. It should be noted that a small amount of terminal olefin products derived from ethenolysis of the seed oil derivatives was generated during each reaction.



Scheme 1: Syntheses of pheromones **2.3** and **2.6**.

In order to investigate the mechanism of formation of pheromone cross products, the reaction of 1-hexene and oleyl alcohol (**2.2**) to produce **2.3** was monitored over time using quantitative ^{13}C NMR (Figure 2). As shown, **2.2** quickly converted to the terminal olefin, 9-decenol, through an ethenolysis reaction. Formation of a ruthenium methylidene is thus required and we surmised that this species was generated from homodimerization of 1-hexene. The resulting 9-decenol then slowly reacted with 1-hexene to produce the desired pheromone cross product **2.3**; the *cis*:*trans* ratio of **2.3** was also monitored and did not change to any appreciable extent over the course of the reaction. It is proposed that internal olefins cannot react directly to produce the desired cross products, but must first be converted to the corresponding terminal olefins via ethenolysis, and only then can they undergo a cross metathesis reaction with another terminal olefin. In order to test this assertion, the internal olefins *cis*-5-decene and **2.4** were reacted in the presence of catalyst **2.1** to produce compound **2.5**. If the proposition was true, since a methylidene cannot be formed due to the absence of ethylene and terminal olefins, there should be no conversion to the desired cross product because the internal olefins cannot be degraded. Indeed, reacting the two internal olefins for up to 19 hours led to no formation of **2.5**, as monitored by gas chromatography; this unique phenomenon will be further explored in Chapter 3.

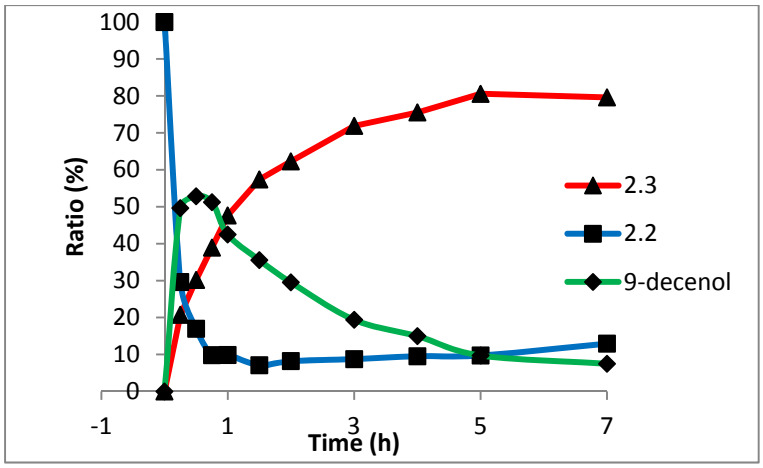
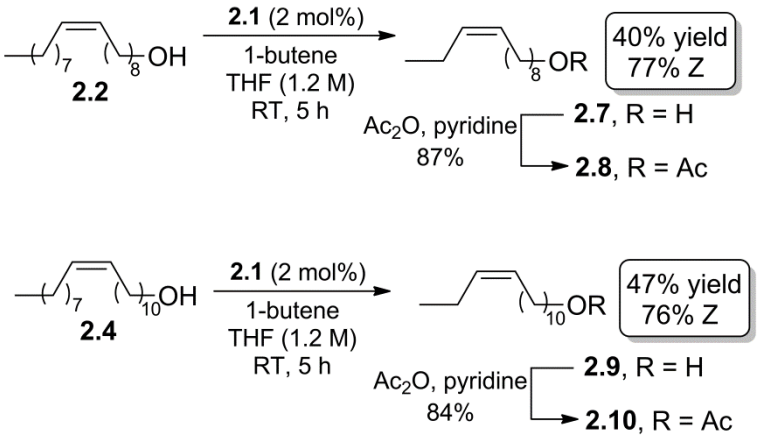


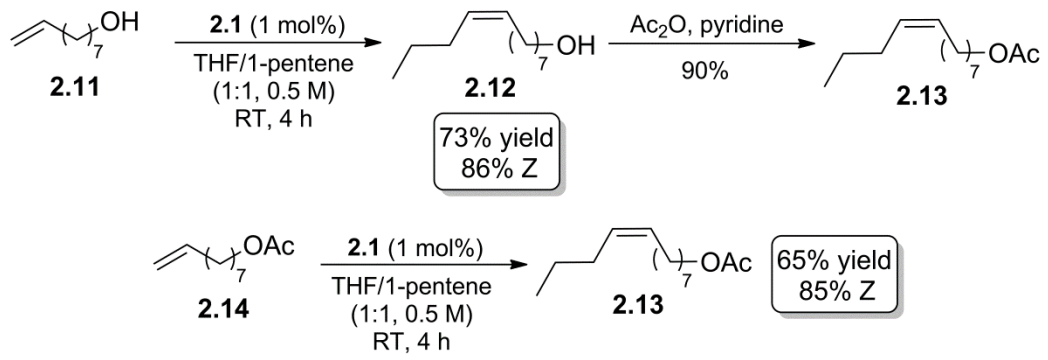
Figure 2: Time course experiment monitoring the relative amounts of **2.2**, 9-decenol, and the desired pheromone **2.3**.

Cross metathesis reactions of the same seed oil derivatives with 1-butene proved to be more difficult than with 1-hexene (Scheme 2). Because gaseous ethylene generated during the reaction must be allowed to escape in order to obtain reasonable conversions, a fixed amount of the gaseous substrate could not be used. The optimal conditions involved slowly bubbling 1-butene through the reaction solution, and slightly higher catalyst loading of **2.1** (2 mol %). Reaction of 1-butene with oleyl alcohol and 11-eicosenol, followed by acetylation of the cross products led to formation of pheromones **2.8** and **2.10** in modest yields (40-47%) and slightly reduced *cis*-selectivity (76-77%).[11] A significant amount of the corresponding terminal olefins derived from ethenolysis of **2.2** and **2.4** was detected, which is not surprising since 1-butene has been used as an ethylene surrogate in alkenolysis reactions.[12]



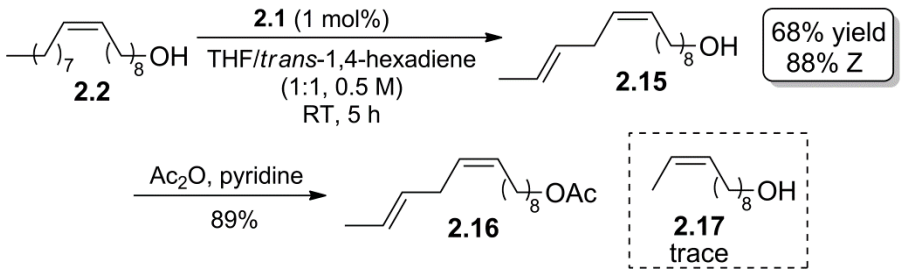
Scheme 2: Syntheses of pheromones **2.8** and **2.10**.

Cross metathesis of the terminal olefins 8-nonenol and 1-pentene led to formation of pheromone **2.12** in good yield (73%) with high *cis*-selectivity (86%) (Scheme 3). Subsequent acetylation of **2.12** provided pheromone **2.13** in 66% overall yield. Compound **2.13** was alternatively synthesized by the direct reaction of 8-nonenyl acetate and 1-pentene which proceeded in analogous overall yields (~65%) and *Z*-selectivities (~85%) when compared to the above two step sequence. The reaction of 1-pentene with 8-nonenol resulted in slightly higher yields compared to the reaction with 8-nonenyl acetate, which is likely a result of the higher selectivity alcohol-containing substrates exhibit for formation of the desired cross products.[13] Regardless, it has been demonstrated that *Z*-olefins with acetate functionality can be easily prepared using catalyst **2.1**. The successful use of functionalized terminal olefins in this methodology is attractive due to the wide variety of commercially available α-olefins containing alcohol and acetate functional groups.



Scheme 3: Syntheses of pheromones **2.12** and **2.13**.

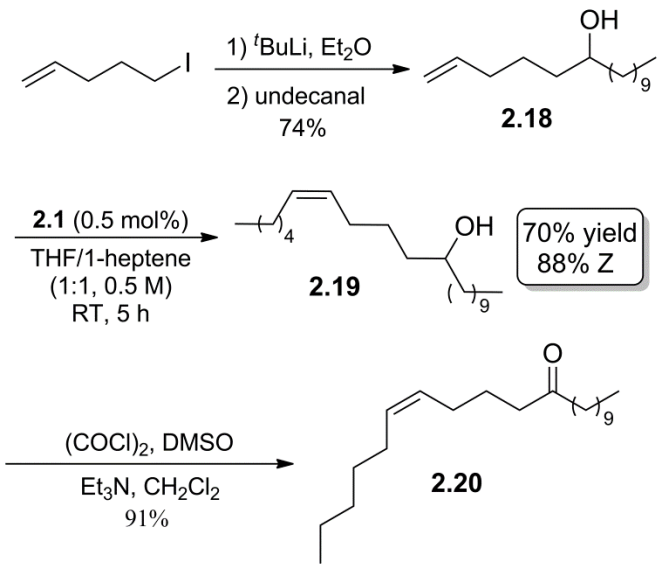
We next attempted to synthesize a pheromone containing an unconjugated diene and were pleased to find that the *Z*-selective cross metathesis of oleyl alcohol and *trans*-1,4-hexadiene using catalyst **2.1** led to selective formation of compound **2.15**, which was subsequently acetylated to yield pheromone **2.16** (Scheme 4). Previous reported syntheses of **2.16** require at least six steps from commercially available starting materials.[14] We were able to synthesize **2.16** starting from renewable and inexpensive reagents in two steps with good overall yield (60%) and high *cis*-selectivity (88%). It should be noted that only trace amounts of products derived from metathesis of the internal double bond of the *trans*-1,4-hexadiene starting material, such as compound **2.17**, were detected. Despite significant research efforts, the selective synthesis of unconjugated and conjugated dienes using previous generations of metathesis catalysts has remained difficult.[15] This is the first example of the cross metathesis of an unconjugated dienes that exhibits chemoselectivity based on olefin geometry.[16] The observed chemoselectivity suggests that this could be a powerful and general tool to construct (*E*,*Z*) dienes. The selective formation of **2.15** over **2.17** seems to be a consequence of the inability of **2.1** to react with 1,2-disubsituted *trans*-olefins.



Scheme 4: Synthesis of unconjugated diene pheromone **2.16**.

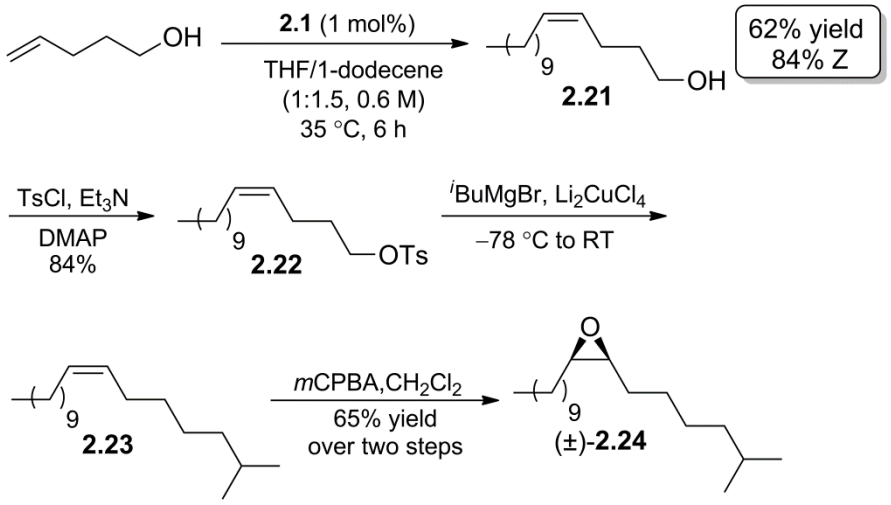
Two of the synthetic targets do not follow the general definition of lepidopteran insect pheromones: the major component pheromone of the Douglas fir tussock moth (**2.20**) contains ketone functionality, while the gypsy moth pheromone disparlure (**2.24**) contains a *cis*-epoxide. We surmised that both pheromones would require more involved syntheses compared to the above compounds, but could be readily accessible using this *Z*-selective metathesis methodology.

A number of syntheses of **2.20** have been reported using as few as four steps, however construction of the *cis*-olefin was predominantly achieved by the partial hydrogenation of alkynes with a Lindlar catalyst or the Wittig reaction.[17] Our synthesis of **2.20** was carried out as shown in Scheme 5. Secondary alcohol **2.18**, formed by the addition of 4-pentenyl lithium to 10-undecenal, was subsequently reacted with 1-heptene in a *Z*-selective cross metathesis reaction with 0.5 mol % catalyst loading of **2.1** to yield **2.19** in good yield (70%) with high *Z*-selectivity (88%). This was then oxidized to the desired ketone-containing pheromone **2.20** using a Swern reaction with 47% overall yield and 88% of the *Z*-olefin and in three steps from commercially available starting materials.



Scheme 5: Synthesis of pheromone **2.20**.

Many routes to enantiopure **2.24** have been reported, and isolation of these compounds has led to determination that (+)-**2.24** is significantly more active than (−)-**2.24** as a chemical attractant. Despite this, the racemic form, (±)-**2.24**, has been shown to disrupt mating as effectively as (+)-**2.24** and is extensively employed in pest control practices.[18] Multiple reported syntheses of (±)-**2.24** exist, all proceeding through the alkyl intermediate **2.23**, and require no fewer than four steps.[19] Our synthesis was carried out as shown in Scheme 6. First, cross metathesis of 4-pentenol and 1-dodecene afforded **2.21** in moderate yield (62%) and high *Z*-selectivity (84%).[20] Alcohol **2.21** was tosylated and subsequently reacted with isobutylmagnesium bromide to produce the desired aliphatic intermediate **2.23**.[21] Subsequent epoxidation of **2.23** with mCPBA yielded species (±)-**2.24** in four overall steps from commercially available starting materials.



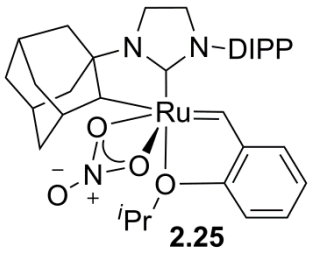
Scheme 6: Synthesis of pheromone (±)-**2.24**.

In summary, the facile synthesis of nine lepidopteran female sex pheromones has been achieved using ruthenium-based *Z*-selective olefin metathesis. The pheromones initially targeted are approved by the EPA as pest control agents, however it is envisioned that other comparable pheromones could be synthesized in a similar manner, further promoting their use as insecticide alternatives. While synthesizing such compounds, we were able to concurrently investigate the reactivity of *Z*-selective catalyst **2.1** in cross metathesis reactions; the mechanism of formation of cross products using **2.1** is markedly different from the mechanism of previous generations of metathesis catalysts (see Chapter 3). In order to better understand the reaction mechanism, the formation of product **2.3** was monitored over time. It was discovered that the internal olefin derivative oleyl alcohol was quickly converted to 9-decenol via ethenolysis before it could react with 1-hexene to produce the desired product. It seems that two internal olefins cannot be reacted with each other to produce a cross product, but must be broken up first by reaction with a ruthenium methylidene; we believe this is a general feature of cross metathesis reactions using catalyst **2.1** which will be discussed in more detail in Chapter 3.

It has been demonstrated that ruthenium-based *Z*-selective metathesis provides an attractive route to form heterodimeric products in good yields with high *cis*-selectivity, and

should emerge as a viable replacement for other inefficient methods used to form *cis*-olefins such as the partial hydrogenation of alkynes and the Wittig reaction, among others. Compounds with a wide variety of functionality, including alcohols, acetates, aldehydes, ketones, and epoxides were easily prepared in a minimal amount of steps from commercial sources, including a number of seed oil derivatives. In fact, the syntheses described above are the most concise for all pheromones reported in this manuscript. As such, it is envisioned that these syntheses can be adapted for industrial scale syntheses and effectively lower the high costs associated with synthetic lepidopteran sex pheromones, leading to the broader adoption of these promising pest control strategies.

After the discovery of catalyst **2.25** that exhibited increased turnover numbers and *Z*-selectivity in homodimerization reactions, it was evaluated in more complicated olefin cross metathesis reactions (Figure 3).[22] The reaction of 1-hexene and 8-nonenyl acetate to form the corresponding pheromone cross product was carried out using catalyst **2.1**, and proceeded in good yield (67%) with high *Z*-selectivity (91%) at a low catalyst loading (0.5 mol %). In contrast, catalyst **2.25** was able to catalyze this transformation with no observable formation of the *E*-isomer and in slightly higher yield (71%) at the same catalyst loading. Additionally, the catalyst loading could be lowered to 0.1 mol % and still provide a good yield of the cross product (60%) while maintaining >98% *Z*-selectivity. The expansion of this methodology to produce more complicated cross products with presumably complete *Z*-selectivity should further enable the use of catalyst **2.25** in the synthesis of *Z*-olefin-containing pheromones and other natural products.

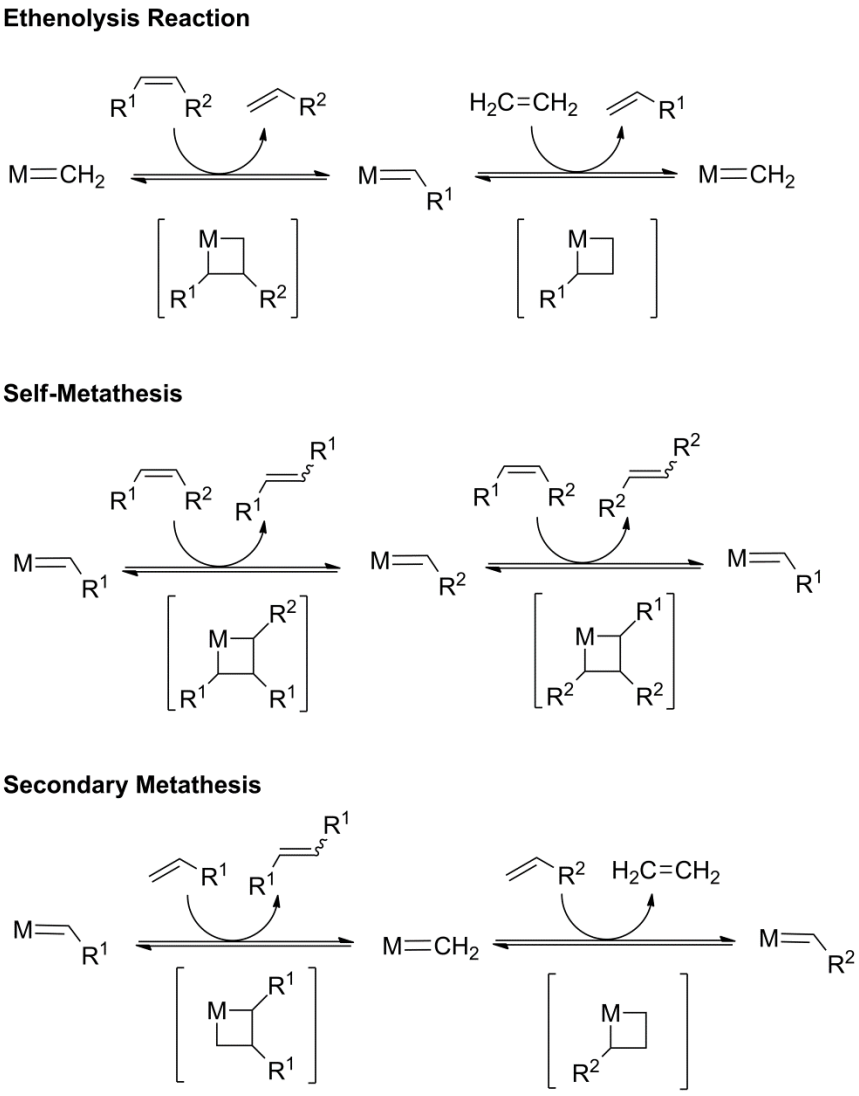


2.25

Figure 3: Highly active and *Z*-selective catalyst **2.25**.

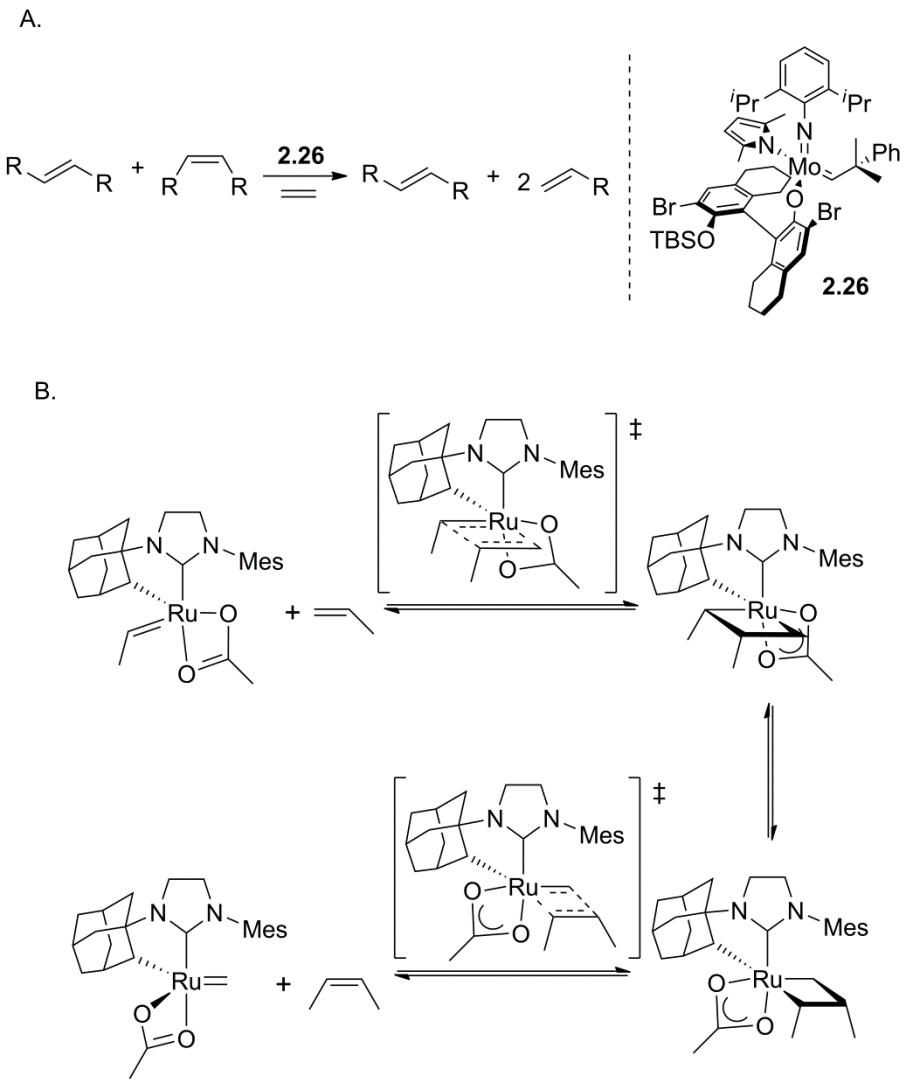
SYNTHESIS OF HIGHLY *E*-OLEFIN ISOMERS USING *Z*-SELECTIVE ETHENOLYSIS:

In order for a metathesis catalyst to be active in ethenolysis reactions, it must exhibit high activity and stability as a propagating methylidene. Unfortunately, many known metathesis catalysts are unstable as methylidene complexes, undergoing rapid decomposition, and thus exhibit poor ethenolysis reactivity.[23] A representative ethenolysis catalytic cycle is depicted in Scheme 7. Initial reaction of an internal olefin with a metal methylidene proceeds via a 1,2-metallacycle and produces a terminal olefin and the corresponding substituted metal alkylidene. Further reaction with ethylene forms a second equivalent of terminal olefin and regenerates the catalytically active methylidene. For an ethenolysis catalyst to show high selectivity at appropriate ethylene pressures, formation of terminal olefin products must be favored over back reactions and side reactions that produce internal olefins (Scheme 7). Side reactions that reduce selectivity for the desired terminal olefin products include self-metathesis and secondary metathesis. Self-metathesis is when a metathesis reaction occurs between two substrate molecules instead of between a substrate molecule and ethylene, and secondary metathesis involves the CM of two terminal olefins to generate an internal olefin and ethylene (Scheme 7). Industrially, the ethenolysis of seed oil derivatives affords chemically desirable products with applications in cosmetics, detergents, polymer additives, and renewable biofuels.[24]



Scheme 7: Ethenolysis and related side reactions.

A particular *Z*-selective molybdenum catalyst (**2.26**) was shown to be effective for the *Z*-selective ethenolysis of internal olefins.[25] In this process, the corresponding molybdenum methylidene reacts preferentially with *cis*-olefins to produce two terminal olefins, while *trans*-olefins react to a significantly smaller extent (Scheme 8). Since ethenolysis is the reverse of cross metathesis, the same 1,2-disubstituted metallacyclobutane complex must be formed as an intermediate in both reactions. Hence, if a catalyst is highly *Z*-selective when forming cross products, it is expected to also be able to selectively degrade *cis*-olefins by ethenolysis, assuming that the corresponding metal methylidene complex is stable (Scheme 8B).



Scheme 8. *Z*-selective ethenolysis.

The family of functional group tolerant *Z*-selective ruthenium-based catalysts reported by our laboratory was thus evaluated to gauge ethenolysis reactivity and selectivity (Figure 4).[6] Catalyst **2.27** is derived from C-H activation of the benzylic position of an *N*-mesityl substituent and thus contains a six-membered chelated structure that imparts slightly improved *Z*-selectivity compared to previous generations of ruthenium catalysts. Catalysts **2.28** and **2.1** contain five-membered chelates derived from C-H activation of an *N*-adamantyl substituent. Our groups and others have

used density functional theory (DFT) calculations to elucidate important information about the mechanism of action, origin of *Z*-selectivity, and stability of chelated ruthenium catalysts **2.1**, **2.27**, **2.28**.[26] The metathesis reaction seems to occur via a side-bound mechanism, different from that with non-chelated ruthenium catalysts, with the olefin approaching *cis* to the NHC ligand on the catalyst.[27] The *N*-adamantyl chelating group positions the *N*-mesityl substituent directly over the forming metallacyclobutane, thus causing its substituents to be oriented away to avoid steric repulsions and leading to high *Z*-selectivity of the metathesis products.

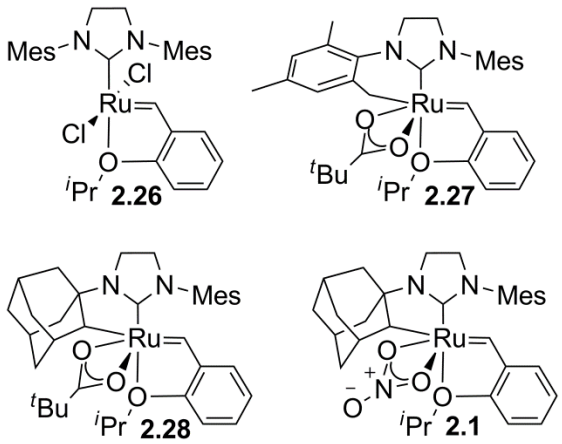
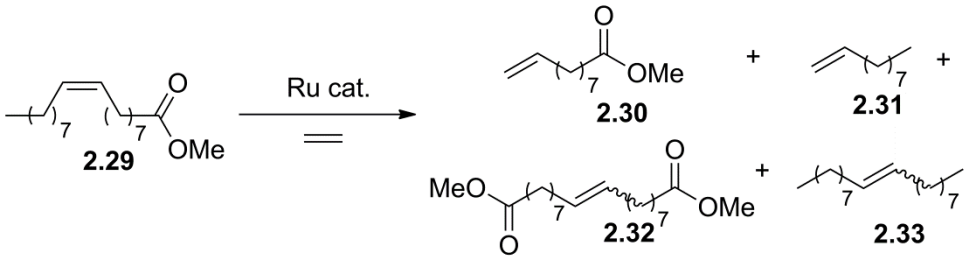


Figure 4. Prominent ruthenium metathesis catalysts.

In order to design better catalysts for *Z*-selective metathesis, a more thorough understanding of this family of chelated ruthenium catalysts is required. The goal of this study is to explore the *Z*-selectivity of these catalysts for ethenolysis reactions and concurrently investigate how this can help us better understand their CM reactivity. The stability and structure of metallacyclobutane intermediates greatly influences metathesis reactivity and selectivity, thus we sought to study the effects of substitution on relevant ruthenacyclobutane intermediates using experimental and theoretical techniques. Both catalyst **2.27**, with a six-membered chelating architecture, and **2.1**,

with a five-membered chelate, were tested so that the effects of chelate size could be investigated.[28] Herein, we report a method for the functional group tolerant *Z*-selective ethenolysis of internal olefins.

We first explored the activity of chelated ruthenium complexes **2.27** and **2.1** for the ethenolysis of the completely *cis*-olefin substrate, methyl oleate (Table 1). The ethenolysis of methyl oleate (**2.29**) is a standard assay used to compare ethenolysis reactivity and selectivity of metathesis catalysts. It should be noted that selectivity here refers to the formation of the desired ethenolysis products, terminal olefins **2.30** and **2.31**, and not to the catalyst's *E*/*Z*-selectivity. Although catalyst **2.27** showed no reactivity at the catalyst loadings tested, catalyst **2.1** was able to catalyze the transformation with high turnovers and high selectivity at low loadings.[29] The fact that **2.1** is highly active as an ethenolysis catalyst and previously exhibited high *Z*-selectivity in CM reactions strongly suggests that it would exhibit high selectivity for *Z*-olefins in ethenolysis reactions.

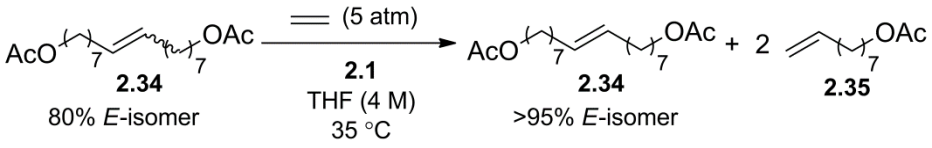


entry[a]	catalyst	mol %	yield[b]	selectivity[c]	TON[d]
1	**2.27**	0.1	0%	-	0
2	**2.27**	0.01	0%	-	0
3	**2.1**	0.1	80%	>95%	800
4	**2.1**	0.01	12%	>95%	1160

Table 1**.** Ethenolysis reactions of methyl oleate catalyzed by catalysts **2.27** and **2.1**. [a] The reactions were run in a minimal amount of CH_2Cl_2 for 1 h at 40 °C and 10.2 atm of ethylene. [b]

Yield = (moles of ethenolysis products **2.30** + **2.31**)*100%/(initial moles of **2.29**). [c] Selectivity = (moles of ethenolysis products **2.30** + **2.31**) *100%/(moles of total products **2.30** + **2.31** + **2.32** + **2.33**). [d] TON = yield*[(moles of **2.29**)/(moles of catalyst)].

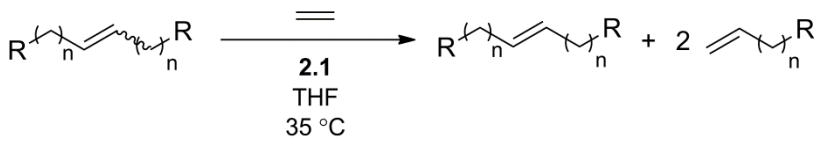
We next tested chelated catalysts **2.27** and **2.1** in the ethenolysis of ~ 4:1 mixtures of the *trans*- and *cis*- isomers of two internal olefins, 5-decene and the acetate-substituted substrate **2.34**, to determine if these catalysts exhibited particular selectivity for *Z*-olefins. We were pleased to find that under the optimized conditions depicted in Scheme 9, catalyst **2.5** was able to enrich both internal olefin mixtures (~80% *E*) to >95% of the *E*-isomer at 5 atm of ethylene and 0.5 mol % catalyst loading for the two substrates (Scheme 9); the products of both reactions were recovered by flash column chromatography.[30] For 5-decene, the purely *E*- isomer (>95% *E*) was isolated in 90% yield based upon initial *E*-content.[31] For **2.34**, the purely *E*-internal olefin (>95% *E*) and 8-nonenyl acetate produced by ethenolysis of the *Z*-olefins were both quantitatively recovered (Scheme 9). Exposure of catalyst **2.27** (0.5 mol %) to a ~ 4:1 mixture of the *trans*- and *cis*- isomers of **2.34** at 5 atm of ethylene led to a very small amount of ethenolysis (<3% conversion) and no observable selectivity. Additionally, only olefin migration of the starting material **2.34** was observed when the reaction was carried out at 1 atm of ethylene at higher loadings of catalyst **2.27** (5 mol %).



Scheme 9. *Z*-selective ethenolysis reaction of substrate **2.34**.

With the knowledge that **2.1** was an effective *Z*-selective ethenolysis catalyst, we sought to investigate its functional group compatibility in *E*-isomer enrichment reactions.[32] A variety of

functional groups were tolerated under the reaction conditions, including acetates, alcohols, esters, amines, and ketones (Table 2). Reaction performed with 5 atm of ethylene for all *E*-dominant substrates (79-82% *E*) led to enrichment of the internal olefins with >95% of the *E*-isomer as monitored by ^{1}H NMR. Although the same reactions performed under 1 atm of ethylene proceeded with high selectivity, reaction at 5 atm was necessary to push the ~80% mixtures to >95% of the *E*-isomer.



entry	compound	R; *n*	initial %*E*	mol % 2.1		pressure (atm)	time (h)	final %*E*
1	**2.36**	CH_3; 3	79	0.5	1		4	90
2			79	0.5	5		4	>95
3			52	0.5	5		4	90
4	**2.34**	OAc; 7	78	0.5	1		4	93
5			78	0.5	5		4	>95
6	**2.37**	OH; 4	82	0.5	1		4	92
7			82	0.5	5		4	>95
8			68	0.5	5		4	90
9	**2.38**	CO_2Me; 6	80	0.5	1		6	88
10			80	0.5	5		6	>95
11	**2.39**	NHPh; 3	80	0.5	1		4	92
12			80	1.0	5		4	>95
13			60	1.0	5		6	86
14	**2.40**	C(O)Me; 2	72	0.5	1		4	90

15	72	0.5	5	4	>95

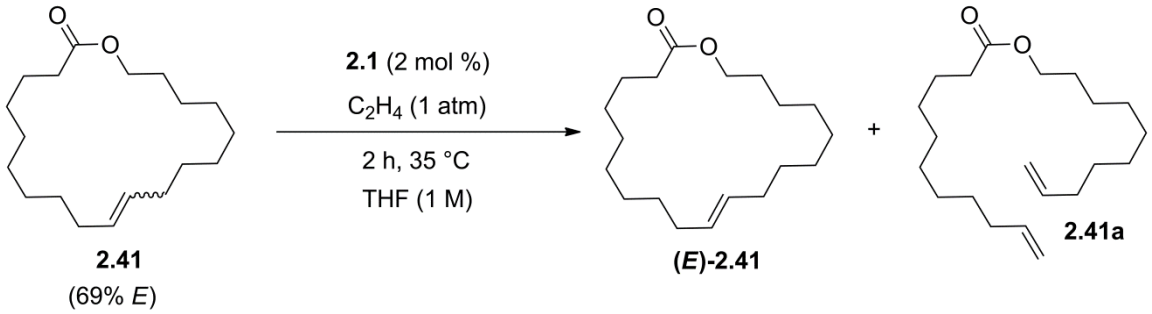
Table 2. *E*-isomer enrichment by *Z*-selective ethenolysis of various functionalized symmetrical internal olefins with the formula $R(CH_2)_nCH=CH-(CH_2)_nR$ using catalyst **2.1**.

SYNTHESIS OF HIGHLY *Z*- AND HIGHLY *E*-MACROCYCLES:

The macrocycle motif is prevalent in a large number of natural products, pharmaceuticals, and musk fragrances. In general, the formation of large rings by macrocyclic ring closing metathesis reactions of acyclic diene starting materials is a more difficult transformation compared to intermolecular cross metathesis or ring closing metathesis of small rings. In order to prevent oligomerization of the acyclic diene starting material, the reactions must be run at low concentration: consequently, higher catalyst loadings are necessary. Additionally, for medium- to large-sized ring systems in which both *E*- and *Z*-isomers are accessible, it is difficult to control or predict the olefin geometry of the products. Following the discovery of NHC-chelated ruthenium alkylidene catalysts, the synthesis of a number of *Z*-macrocycles with a variety of ring sizes (13 – 20 atoms) containing various functional groups (ester, ketone, alcohol, protected amide) was demonstrated.[33] In general macrocyclic ring closing metathesis reactions proceeded in moderate to good yields (50-75%) and with generally high *Z*-selectivity (75-94%) using catalyst **2.1**. Interestingly, macrocycles containing alcohol or ketone functionality showed increased levels of *Z*-content degradation (as low as 50% *Z* after 24 hours). When catalyst **2.25** was evaluated, macrocyclic products were obtained with very high *Z*-selectivity (>98%), albeit in diminished yields.

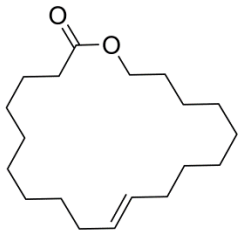
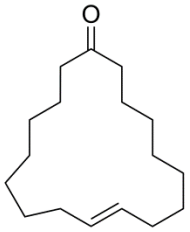
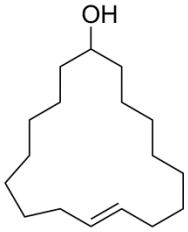
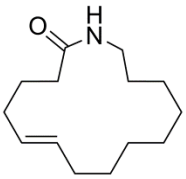
In a complementary approach to the synthesis of the *Z*-macrocycles, we were also able to further exploit catalyst **2.1** for the isolation of purely *E*-macrocycles, through the selective degradation of the *Z*-isomer in the corresponding *E*-dominant mixtures (Scheme 10). Ring-opening via ethenolysis is simply the reverse of the macrocyclic ring closing metathesis reaction.

Thus, since high *Z*-selectivity was evidenced in the forward reaction, it was expected that the reverse reaction would also display high selectivity for *Z*-olefins. Indeed, exposure of an *E*/*Z* mixture of lactone 6 (69% E) to ethylene (1 atm) in the presence of catalyst **2.1** (2 mol%) led to the complete degradation of **(*Z*)-2.41** after only 2 hours at 35 °C (Scheme 10). Notably only an atmospheric pressure of ethylene was necessary. It is also significant to mention that the corresponding ring-opened diene (**2.41a**) was also recovered, and thus could subsequently be recycled in subsequent macrocyclic ring closing metathesis reactions if desired.



Scheme 10. *Z*-Selective ethenolysis of highly *E*-macrocycle **2.41**.

We were able to apply similar reaction conditions to macrocycles containing ketone (**2.42**), alcohol (**2.43**), and amide (**2.44**) functionality (Table 3). In general, complete consumption of the *Z*-macrocycle occurred within two hours, affording the pure *E*-macrocycle in good yield. The lower yield of ketone-containing product **2.42** is likely a result of the elevated temperature required to form the *E*-isomer exclusively, which might also be expected to accelerate undesired degradation of the *E*-macrocycle. Additionally, an increase in oligomerization was also observed in this case, thus reducing the yield of the recovered diene.

Compound	Initial (*E*) (%)	Final (*E*) (%)[a]	Yield (%)[b,c]	Compound	Initial (*E*) (%)	Final (*E*) (%)[a]	Yield (%)[b,c]
 **(*E*)-2.41**	69	>95	69 (81)[d]	 **(*E*)-2.42**	80	>95	40 (46)[d]
 **(*E*)-2.43**	80	>95	78 (79)[d]	 **(*E*)-2.44**	55	>95	75 (86)[d]

[a]*E*/*Z* ratios determined by ^{1}H- or ^{13}C-NMR, [b]isolated product, [c]calculated based on recovery from initial (*E*)/(*Z*) mixture, [d]recovered diene, from ethenolysis of macrocyclic olefin

Table 3. *Z*-Selective ethenolysis of a mixture of *E*-dominant macrocycles.

SYNTHESIS OF HIGH VALUE PRODUCTS FROM SOYBEAN OIL:

The use of seed oils as raw materials for chemical synthesis has gained increasing popularity in recent years and ruthenium-catalyzed olefin metathesis has emerged as a powerful tool for seed oil conversion.[34] This is partially due to the high moisture, air, and functional group sensitivity of ruthenium metathesis catalysts. The generation of valuable starting materials from seed oils for the synthesis of insect pheromones and macrocyclic musk fragrances would be highly desired for their cost-effective, industrial scale syntheses. Accordingly, recent efforts have been aimed at converting soybean oil into functionalized and unfunctionalized hydrocarbons.

Soybean oil is comprised of triacylglycerides that contain mono-, di-, and tri-unsaturated side chains (Figure 5). The side chain depicted in red is linolenic acid which contains an unconjugated triene motif and the side chain depicted in green in linoleic acid which contains an

unconjugated diene; the side chain in blue is the monounsaturated oleic acid. It was proposed that reaction of propylene with the unconjugated polyenes of linolenic and linoleic acid in the presence of a ruthenium metathesis catalyst could yield *trans*-1,4-hexadiene, a starting material used in the synthesis of the *E*,*Z*-unconjugated diene pheromone **2.16** (Scheme 11). At 45 psi of propylene, 60 °C, and 500 ppm of catalyst **2.45**, the propenolysis reaction generated the volatile hydrocarbons shown in Scheme 11. A large proportion of 1,4-cyclohexadiene was formed, which was presumably due to homodimerization and ring closure of the conjugated diene products at the low propylene pressure (45 psi) and high temperature (60 °C) under investigation. Increasing the propylene pressure to 140 psi and decreasing the temperature to 25 °C allowed for selective formation of the unconjugated diene products with only trace amounts of 1,4-cyclohexadiene formed. The volatile organic compounds could then be purified by distillation.

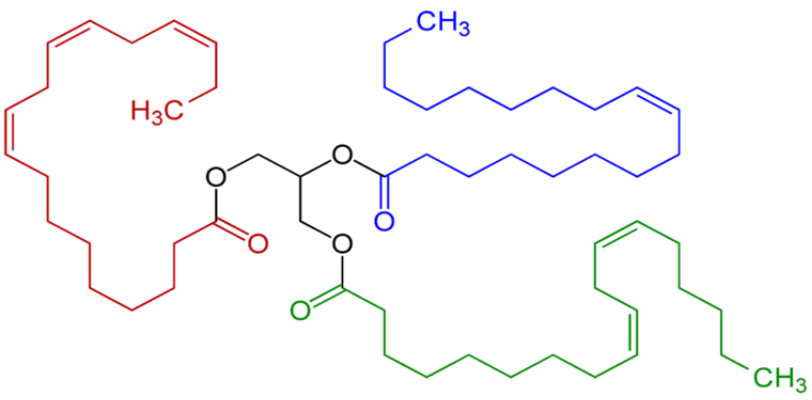
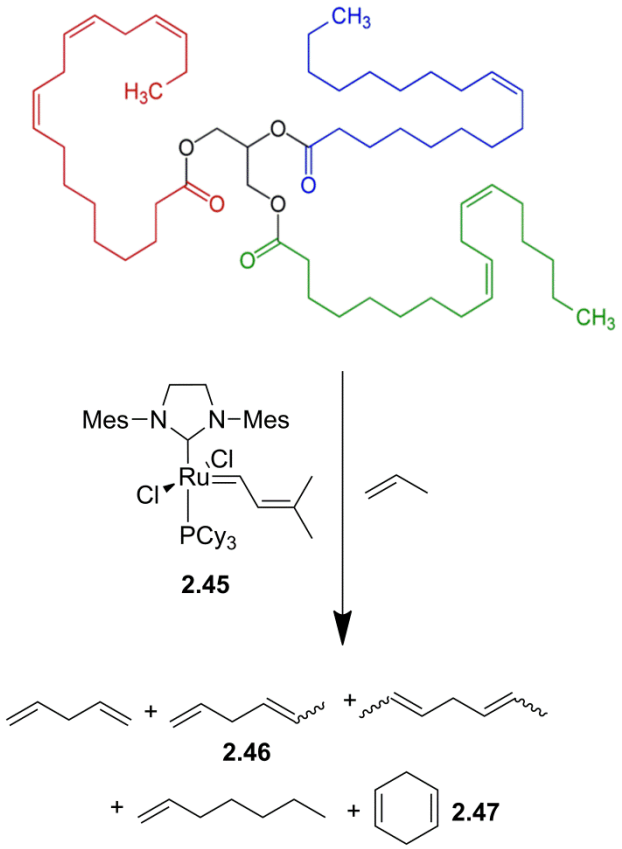


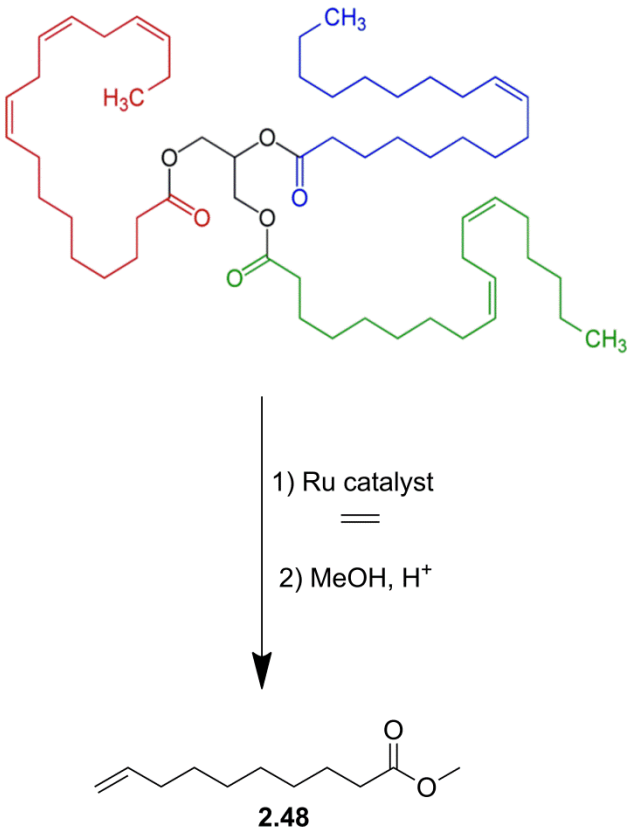
Figure 5: Representative triglyceride of soybean oil.



Scheme 11: Propenolysis of soybean oil for the production of high value products.

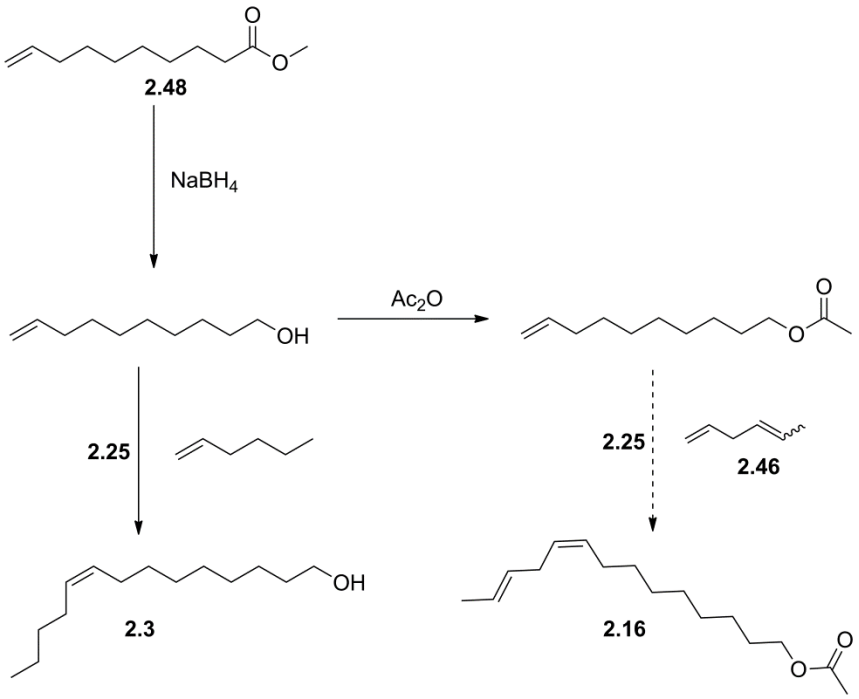
Valuable products have also been isolated through ruthenium-catalyzed ethenolysis and transesterification of soybean oil.[35] Methyl-9-decenoate (**2.48**) was synthesized according to the route shown in Scheme 12. We envisioned that this could be a valuable starting material for the formation of different pheromones and macrocycles. Reduction of **2.48** with $NaBH_4$ led to the formation of the corresponding primary alcohol which was reacted with highly active and *Z*-selective catalyst **2.25** to yield pheromone **2.3** (Scheme 13). The terminal olefin alcohol was then acetylated and it is envisioned that it could be reacted with the *trans*-1,4-hexadiene generated above to yield unconjugated diene pheromone **2.16** using *Z*-selective olefin metathesis. Additionally, compound **2.48** could be homodimerized using catalyst **2.25** and subsequently reacted in Dieckmann condensation and decarboxyalation reactions, according to a reported

procedure, to yield the popular musk fragrance civetone (**2.42** in Scheme 14). A related macrocyclic musk, yuzu lactone (**2.49**), could be produced by the reaction of methyl ester **2.48** with 3-butenol to afford an acyclic diene that could subsequently be reacted with catalyst **2.25** in a macrocyclic ring closure reaction. It is envisioned that all of these products will be formed with near perfect selectivity for the *Z*-olefin isomer and will showcase the prominent Z-selective metathesis reactions reported by our group: cross metathesis, diene-selective cross metathesis, terminal olefin homodimerization, and macrocyclic ring closing metathesis.

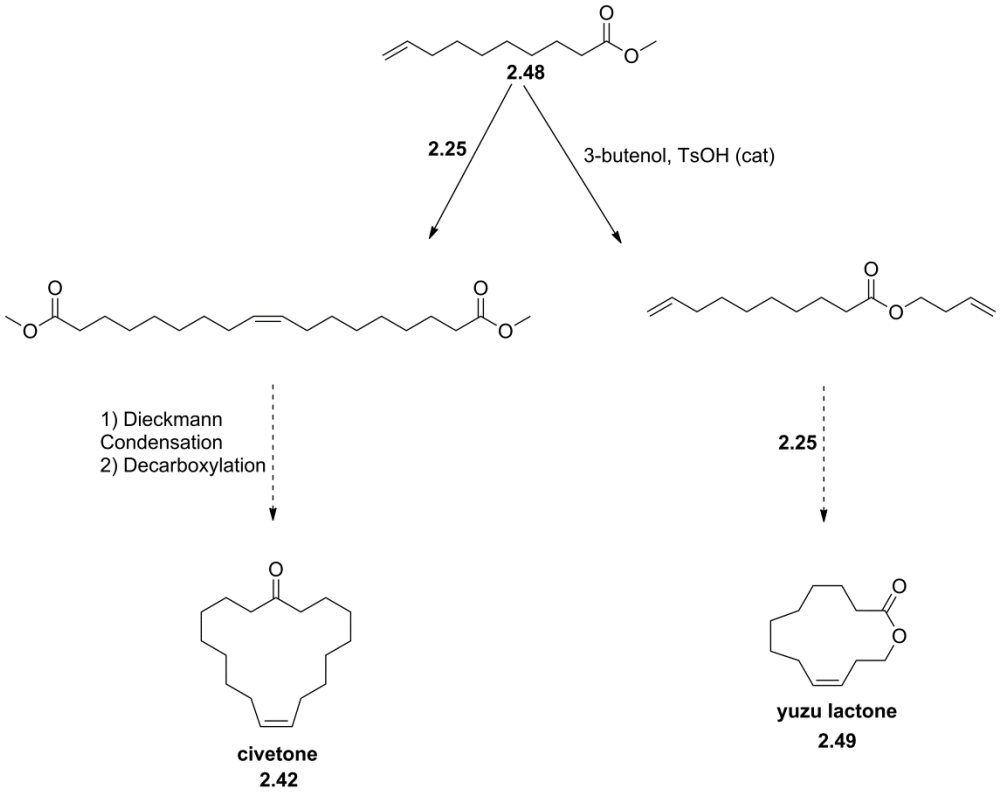


2.48

Scheme 12: Ethenolysis of soybean oil to produce high value products.



Scheme 13: Generation of insect pheromones from soybean oil derived compound **2.48**.



Scheme 14: Generation of macrocyclic musk fragrances from soybean oil derived compound **2.48**.

CONCLUSIONS:

Olefin metathesis has become a powerful and ubiquitous tool for synthetic chemists mainly because it has been used to synthesize a diverse set of products. The formation of *Z*-internal olefins using functional group tolerant NHC-chelated ruthenium alkylidene catalysts has only recently been reported and, in order to demonstrate its utility as a powerful synthetic tool, the synthesis of natural products bearing or derived from *Z*-olefins was attempted. It was found that a variety of Lepidopteran insect female sex pheromones could be synthesized in a facile manner using *Z*-selective olefin cross metathesis: these types of compounds have been used extensively in pest control practices as alternatives to highly toxic insecticides. Additionally, using *Z*-selective macrocyclic ring closing metathesis, macrocyclic musk natural products used extensively in the fragrance industry were formed in modest yields and with high *Z*-selectivity.

As a complementary approach for the formation of *Z*-olefins, the *Z*-selective ethenolysis reactivity of our family of NHC-chelated catalysts was investigated for the selective degradation of *Z*-olefins. It was discovered that upon treatment of stereoisomeric mixtures of *E*- and *Z*-olefins with ethylene, the *Z*-isomer was selectively degraded to the corresponding terminal olefins, providing enrichment of the *E*-isomer at low catalyst loadings and ethylene pressures. This process exhibited high functional group tolerance and worked for linear and macrocyclic internal olefins. Now, in addition to being able to form *Z*-olefin-containing natural products with near perfect *Z*-selectivity using NHC-chelated catalysts, we have discovered a technique to convert stereoisomeric mixtures of internal olefins to the purely *E*-isomers using the same catalysts and with high functional group tolerance. Accordingly, it is envisioned that these catalysts will find utility in the synthesis of increasingly more complex natural and unnatural products.

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7 produced analogous yields and *Z*-selectivities when compared to the reaction of oleyl alcohol and 1-butene.

13. A much larger amount of the undesired homodimer was detected for reaction of 8-nonenyl acetate compared to 8-nonenol.

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28. Previous experiments have shown that catalyst **28** is unstable to excess ethylene and thus was not investigated in this study.

29. Catalyst **2.1** exhibits smaller turnover numbers for ethenolysis when compared to the state of the art ruthenium, molybdenum, and tungsten catalysts: a) Anderson, D. R.; Ung, T.; Mkrtumyan, G.; Bertrand, G.; Grubbs, R. H.; Schrodi, Y. *Organometallics*, **2008**, *27*, 563. b) Thomas, R. M.; Keitz, B. K.; Champagne, T. M.; Grubbs, R. H. *J. Am. Chem. Soc*. **2011**, *133*, 7490. (c) Marinescu, S. C.; Schrock. R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc*. **2009**, *131*, 10840.

30. The yields reported herein were calculated based on the assumption that only the *Z*-internal olefin isomer underwent ethenolysis and that it reacted completely.

31. It should be noted that the volatility of the generated 1-hexene prevented it from being recovered and it was thus removed *in vacuo*.

32. The reactions depicted in table 2 were performed to showcase the functional group tolerance of this method and the final %*E*. Isolated yields of highly %*E* products were obtained for two of the substrates (see Experimental), **2.34** (96% yield, >95%*E*) and **2.36** (90% yield, >95%*E*).

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34. Schrodi, Y., Ung, T., Vargas, A., Mkrtumyan, G., Lee, C. W., Champagne, T. M., Pederson, R. L. and Hong, S. H. *Clean Soil Air Water* **2008**, *36*, 669.

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Experimental Section:

General methods

All reactions were carried out in dry glassware under an argon atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres Glovebox under a nitrogen atmosphere, unless otherwise specified. All solvents were purified by passage through solvent purification columns and further degassed by bubbling argon. NMR solvents were dried over CaH_2 and vacuum transferred to a dry Schlenk flask and subsequently degassed with bubbling argon. C_6D_6 was purified by passage through a solvent purification column. $CDCl_3$ was used as received. All α-olefins were filtered through a plug of neutral alumina prior to use. Ruthenium complex 1 was obtained from Materia Inc. 11-eiosenol (**2.4**) was synthesized from Jojoba oil.[1] Other commercially available reagents and silica gel were used as received. Benzylidene-bis (tricyclohexylphosphine)dichlororuthenium (**2.50**) and (1,3-Bis(2,4,6-trimethylphenyl)- 2-imidazolidinylidene) dichloro(phenylmethylene)(tricyclohexylphosphine)ruthenium (**2.51**) were obtained from Materia, Inc.

^1H NMR spectra were acquired at 500 MHz and ^{13}C NMR spectra at 125 MHz as $CDCl_3$ solutions unless otherwise noted. Quantitative ^{13}C measurements were acquired at 100 MHz (decoupled, without NOE, 15 second delay time). High-resolution mass spectra (HRMS) were provided by the California Institute of Technology Mass Spectrometry Facility using a JEOL JMS-600H High Resolution Mass Spectrometer. All HRMS were by positive-ion EI or FAB.

All cross metathesis reactions involving the seed oil derivatives **2.2** and **2.4** required purification by multiple columns to separate the desired products from the starting material and any terminal olefins generated.

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[1] R.L. Pederson, I. M. Fellows, T. A. Ung, H. Ishihara, S. P. Hajela, *Adv. Synth. Catal*. **2002**, *344*, 728.

(*Z*)-Tetradec-9-en-1-ol (2.3)

In a glovebox, a 20 mL vial was charged with oleyl alcohol (1.0 g, 3.7 mmol), 1-hexene (4 mL), and THF (4 mL). A solution of **2.1** (0.023 g, 1 mol%) in THF (0.5 mL) was added, and the mixture was stirred in an open vial for 5 hours. The vial was removed from the glovebox, the reaction was quenched with excess ethyl vinyl ether, and the solvent was removed *in vacuo*. Flash chromatography of the residue (SiO_2, using a gradient of hexanes to 20% EtOAc in hexanes) provided **2.3** (0.73 g, 77% yield, 86% *Z* as determined by ^{1}H-NMR) as a colorless oil; ^{1}H NMR ($CDCl_3$): δ 5.35 (2H, m), 3.64 (2H, td, *J* = 6.6, 5.3 Hz), 2.02 (4H, m), 1.57 (2H, m), 1.22-1.39 (15H, m), 0.90 (3H, t, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$): δ 129.9, 129.8, 63.1, 32.8, 32.0, 29.8, 29.5, 29.4, 29.2, 27.2, 26.9, 25.7, 22.4, 14.0; HRMS (FAB): 213.2215, $[C_{14}H_{28}O+H]^+$ requires 213.2218.

(*Z*)-Hexadec-11-en-1-ol (2.5)

According to the procedure for compound **2.3**, 11-eicosenol (1.3 g, 4.4 mmol) and 1-hexene (6 mL) in THF (6 mL) were reacted with **2.1** (0.028 g, 1 mol%) to provide **2.5** (0.84 g, 76% yield, 86% *Z* as determined by ^{1}H-NMR) as a colorless oil; ^{1}H NMR ($CDCl_3$): δ 5.36 (2H, m), 3.64 (2H, td, *J* = 6.5, 5.3 Hz), 2.02 (4H, m), 1.56 (2H, m), 1.23-1.38 (19H, m), 0.90 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$): δ 129.9 (2C), 63.1, 32.8, 32.0, 29.8, 29.6 (2C), 29.5, 29.4, 29.3, 27.2, 26.9, 25.8, 22.4, 14.0; HRMS (FAB): 241.2536, $[C_{16}H_{32}O+H]^+$ requires 241.2531.

(*Z*)-Hexadec-11-enal (2.6)

DMSO (0.11 mL, 1.6 mmol) was added dropwise to a solution of oxalyl chloride (0.080 mL, 0.96 mmol) in CH_2Cl_2 (5 mL) at -78 °C, and after 5 minutes a solution of alcohol **2.5** (0.21 g,

0.87 mmol) in CH_2Cl_2 (0.9 mL) was added. After stirring for 15 minutes at the same temperature, triethylamine (0.61 mL, 4.4 mmol) was added. The mixture was warmed to room temperature, diluted with Et_2O, washed sequentially with 1M HCl, saturated aqueous $NaHCO_3$, brine, dried with Na_2SO_4, and the solvent was removed *in vacuo*. Flash chromatography of the residue (SiO_2, 10% EtOAc in hexanes) provided **2.6** (0.20 g, 95% yield, 86% *Z* as determined by ^{1}H-NMR) as a colorless oil; ^{1}H NMR ($CDCl_3$): δ 9.76 (1H, t, *J* = 1.9 Hz), 5.36 (2H, m), 2.42 (2H, td, *J* = 7.4, 1.9 Hz), 2.02 (4H, m), 1.63 (2H, m), 1.24-1.36 (16H, m), 0.90 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$): δ 202.9, 129.9, 129.8, 43.9, 32.0, 29.8, 29.5, 29.4 (2C), 29.3, 29.2, 27.2, 26.9, 22.4, 22.1, 14.0; HRMS (FAB): 237.2209, $[C_{16}H_{30}O\text{-}H]^+$ requires 237.2218.

(*Z*)-Dodec-9-en-1-ol (2.7)

In a glovebox, a 25 mL Schlenk flask was charged with oleyl alcohol (1.0 g, 3.7 mmol) and THF (2.5 mL). A solution of **2.1** (0.047 g, 2 mol%) in THF (0.5 mL) was added and the container was sealed and removed from the glovebox. The flask was attached to a Schlenk line and after three pump/refill cycles, under a positive pressure of argon, the Teflon plug was removed and replaced with a rubber septum. A needle was introduced into the flask and placed into the reaction solution. A slow bubble of 1-butene was introduced and the reaction was allowed to stir with bubbling 1-butene for 4 hours. The reaction was quenched with excess ethyl vinyl ether, and the solvent was removed *in vacuo*. Flash chromatography of the residue (SiO_2, using a slow gradient of hexanes to 9% EtOAc in hexanes) provided **2.7** (0.27 g, 40% yield, 77% *Z* as determined by ^{13}C-NMR) as a colorless oil; ^{1}H NMR ($CDCl_3$): δ 5.29-5.45 (2H, m), 3.63 (2H, t, *J* = 6.6 Hz), 1.94-2.06 (4H, m), 1.56 (2H, p, *J* = 6.7 Hz), 1.29 (11H, m), 0.95 (3H, m). ^{13}C NMR ($CDCl_3$): δ 131.6, 129.3, 63.1, 32.8, 32.6, 29.8, 29.5, 29.4, 29.2, 29.1, 20.5, 14.4; HRMS (FAB): 184.1830, $[C_{12}H_{24}O]^+$ requires 184.1827.

(Z)-Dodec-9-en-1-yl acetate (2.8)

Acetic anhydride (0.17 mL, 1.8 mmol), then pyridine (90 μL, 1.1 mmol), were added sequentially to alcohol **2.7** (0.17 g, 0.93 mmol) in CH_2Cl_2 (1.8 mL), and stirred at room temperature for 17 hours. The mixture was diluted with diethyl ether, washed with saturated aqueous $NaHCO_3$, then brine, dried with Na_2SO_4, and concentrated. Flash chromatography of the residue (SiO_2, 5% EtOAc in hexanes) provided **2.8** (0.18 g, 87% yield, 74% *Z* as determined by ^{13}C-NMR) as a colorless oil; ^{1}H NMR ($CDCl_3$): δ 5.28-5.43 (2H, m), 4.05 (2H, t, *J* = 6.8 Hz), 2.04 (7H, m), 1.61 (2H, td, *J* = 9.8, 8.7, 4.6 Hz), 1.29 (10H, m), 0.95 (3H, m); ^{13}C NMR ($CDCl_3$): δ 171.3, 131.6, 129.3, 64.7, 32.6, 29.8, 29.5, 29.3, 29.2, 28.7, 26.0, 21.1, 20.6, 14.5; HRMS (FAB): 227.2045, $[C_{14}H_{26}O_2+H]^+$ requires 227.2006.

(*Z*)-Tetradec-11-en-1-ol (2.9)

According to the procedure for compound **2.7**, 11-eicosenol (1.1 g, 3.7 mmol) and THF (3 mL) were reacted with **2.1** (0.047 g, 2 mol%) to provide **2.9** (0.37 g, 47% yield, 76% *Z* as determined by ^{13}C-NMR) as a colorless oil; ^{1}H NMR ($CDCl_3$): δ 5.29-5.45 (2H, m), 3.63 (2H, t, *J* = 6.6 Hz), 1.94-2.06 (4H, m), 1.56 (2H, dt, *J* = 13.5, 6.7 Hz), 1.27, (15H, m), 0.96 (3H, m); ^{13}C NMR ($CDCl_3$): δ 131.7, 129.5, 63.2, 33.0, 29.9, 29.7, 29.7, 29.7, 29.6, 29.4, 27.2, 25.9, 20.7, 14.6; HRMS (FAB): 212.2135, $[C_{14}H_{28}O]^+$ requires 212.2140.

(Z)-Tetradec-11-en-1-yl acetate (2.10)

Acetic anhydride (0.17 mL, 1.8 mmol), then pyridine (86 μL, 1.1 mmol), were added sequentially to alcohol **2.7** (0.19 g, 0.89 mmol) in CH_2Cl_2 (1.8 mL), and stirred at room temperature for 12 hours. The mixture was diluted with diethyl ether, washed with saturated aqueous $NaHCO_3$, then brine, dried with Na_2SO_4, and concentrated. Flash chromatography of the residue (SiO_2, 5% EtOAc in hexanes) provided **2.13** (0.19 g, 84% yield, 77% *Z* as determined by

^{13}C-NMR) as a colorless oil; ^{1}H NMR ($CDCl_3$): δ 5.29-5.43 (2H, m), 4.05 (2H, t, *J* = 6.8 Hz), 2.04 (7H, m), 1.61 (2H, m), 1.27 (14H, m), 0.95 (3H, m); ^{13}C NMR ($CDCl_3$): δ 171.4, 131.7, 129.4, 64.8, 32.7, 29.9, 29.7 (2C), 29.4 (2C), 28.7, 27.2, 26.1, 21.2, 20.7, 14.6; HRMS (FAB): 255.2324, $[C_{16}H_{30}O_2+H]^+$ requires 255.2319.

(*Z*)-Dodec-8-en-1-ol (2.12)

In a glovebox, a 20 mL vial was charged with 8-nonenol (0.58 g, 4.1 mmol), 1-pentene (4 mL), and THF (4 mL). A solution of **2.1** (0.026 g, 1 mol%) in THF (0.5 mL) was added, and the mixture was stirred in an open vial for 4 hours. The vial was removed from the glovebox, the reaction was quenched with excess ethyl vinyl ether, and the solvent was removed *in vacuo*. Flash chromatography of the residue (SiO_2, using a gradient of hexanes to 20% EtOAc in hexanes) provided **2.12** (0.56 g, 73% yield, 86% *Z* as determined by ^{1}H-NMR) as a colorless oil; ^{1}H NMR ($CDCl_3$): δ 5.36 (2H, m), 3.64 (2H, br t, *J* = 5.3 Hz), 2.01 (4H, m), 1.36 (2H, m), 1.28-1.40 (11H, m), 0.90 (3H, t, *J* = 7.4 Hz); ^{13}C NMR ($CDCl_3$): δ 130.0, 129.7, 63.1, 32.8, 29.3 (4C), 27.2, 25.7, 22.9, 13.8; HRMS (EI): 184.1805, $[C_{12}H_{24}O]^+$ requires 184.1827.

(*Z*)-Dodec-8-en-1-yl acetate (2.13)

By cross metathesis of nonenyl acetate: according to the procedure for compound **2.12**, 8-nonenyl acetate (0.76 g, 4.1 mmol) and 1-pentene (4 mL) in THF (4 mL) were reacted with **2.1** (0.026 g, 1 mol%) to provide **2.13** (0.60 g, 65% yield, 85% *Z* as determined by ^{1}H-NMR) as a colorless oil; ^{1}H NMR ($CDCl_3$): δ 5.36 (2H, m), 4.05 (2H, t, *J* = 6.8 Hz), 2.05 (3H, s), 2.01 (4H, m), 1.62 (2H, m), 1.27-1.41 (10H, m), 0.90 (3H, t, *J* = 7.4 Hz); ^{13}C NMR ($CDCl_3$): δ 171.2, 129.9, 129.8, 64.7, 29.7, 29.3, 29.2 (2C), 28.6, 27.2, 25.9, 22.9, 21.0, 13.8; HRMS (EI): 227.2021, $[C_{14}H_{26}O+H]^+$ requires 227.2011.

By acetylation of compound **2.12***:* According to the procedure for compound **2.8**, Ac_2O (0.29 mL, 3.0 mmol), pyridine (0.14 mL, 1.8 mmol), and alcohol **2.12** (0.28 g, 1.5 mmol) were reacted to provide **2.13** (0.19 g, 90% yield, 86% *Z* as determined by ^{1}H-NMR) as a colorless oil.

(9*Z*,12*E*)-Tetradeca-9,12-dien-1-ol (2.15)

According to the procedure for compound **2.3**, oleyl alcohol (1.0 g, 3.7 mmol) and 1,4-*trans*-hexadiene (4 mL) in THF (4 mL) were reacted with **2.1** (0.023 g, 1 mol%) to provide **2.15** (0.53 g, 68% yield, 88% *Z* as determined by ^{1}H-NMR) as a colorless oil; ^{1}H NMR ($CDCl_3$): δ 5.32-5.49 (4H, m), 3.64 (2H, br t, *J* = 6.6 Hz), 2.71 (2H, m), 2.03 (2H, m), 1.03 (3H, m), 1.56 (2H, m), 1.25-1.39 (11H, m); ^{13}C NMR ($CDCl_3$): δ 130.4, 129.6, 127.7, 125.1, 63.1, 32.8, 30.4, 29.6, 29.5, 29.4, 29.2, 27.1, 25.7, 17.9; HRMS (FAB): 209.1906, $[C_{14}H_{26}O\text{-}H]^+$ requires 209.1905.

(9*Z*,12*E*)-T**etradeca-9,12-dien-1-yl acetate (2.16)**

Acetic anhydride (3.1 mmol, 0.29 mL), then pyridine (1.8 mmol, 0.14 mL), were added sequentially to alcohol **2.15** (1.5 mmol, 0.32 g) in CH_2Cl_2 (3 mL), and stirred at room temperature for 18 hours. The mixture was diluted with diethyl ether, washed with saturated aqueous $NaHCO_3$, then brine, dried with Na_2SO_4, and concentrated. Flash chromatography of the residue (SiO_2, 10% EtOAc in hexanes) provided **2.16** (0.34 g, 89% yield, 88% *Z* as determined by ^{1}H-NMR) as a colorless oil; ^{1}H NMR ($CDCl_3$): δ 5.31-5.49 (4H, m), 4.05 (2H, t, *J* = 6.8 Hz), 2.72 (2H, m), 2.05 (3H, s), 2.02 (2H, m), 1.65 (2H, m), 1.61 (2H, m), 1.24-1.38 (11H, m); ^{13}C NMR ($CDCl_3$): δ 171.3, 130.4, 129.6, 127.7, 125.1, 64.7, 30.4, 29.6, 29.4, 29.2 (2C), 28.6, 27.1, 25.9, 21.0, 17.9; HRMS (FAB): 251.2000, $[C_{16}H_{28}O_2\text{-}H]^+$ requires 251.2011.

(*Z*)-Hexadec-1-en-6-ol (2.18)

A solution of *tert*-butyllithium (19 mL, 1.7 M in pentanes) was added dropwise to a -78 °C solution of 5-iodopentene (3.0 g, 15 mmol) in Et_2O (25 mL), which was subsequently warmed to room temperature over 1 hour. The solution was re-cooled to -78 °C, and undecanal (2.4 mL, 12 mmol) was added dropwise. The solution was let to warm to room temperature, washed with saturated $NaHCO_3$ (*aq.*), then brine, dried with Na_2SO_4, and the solvent was removed *in vacuo*. Flash chromatography of the residue (SiO_2, 10% EtOAc in hexanes) yielded **2.18** (4.2 g, 74%) as a colorless solid;^{1}H NMR ($CDCl_3$): δ 5.81 (1H, m), 5.01 (1H, m), 4.95 (1H, m), 3.60 (1H, m), 2.08 (2H, m), 1.37-1.58 (7H, m), 1.22-1.34 (16H, m), 0.88 (3H, t, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$): δ 138.8, 114.6, 71.9, 37.5, 36.9, 33.8, 31.9, 29.7, 29.6 (3C), 29.35, 25.7, 24.9, 22.7, 14.1.

(*Z*)-Henicos-6-en-11-ol (2.19)

According to the procedure for compound **2.15**, compound **2.18** (1.0 g, 4.2 mmol) and 1-heptene (4 mL) in THF (4 mL) were reacted with **2.1** (0.015 g, 0.5 mol%) to provide **2.19** (0.91 g, 70% yield, 88% *Z* as determined by quantitative ^{13}C-NMR) as a colorless oil; ^{1}H NMR ($CDCl_3$): δ 5.36 (2H, m), 3.59 (1H, m), 2.03 (4H, m), 1.21-1.54 (29H, m), 0.88 (6H, m); ^{13}C NMR ($CDCl_3$): δ 130.4, 129.4, 71.9, 37.6, 37.1, 31.9, 31.6, 29.7 (2C), 29.6 (2C), 29.4 (2C), 27.2 (2C), 25.8, 25.7, 22.7, 22.6, 14.1 (2C); HRMS (FAB): 309.3162, $[C_{21}H_{42}O\text{-}H]^+$ requires 309.3157.

(*Z*)-Henicos-6-en-11-one (2.20)

According to the procedure for compound **2.6**, DMSO (0.080 mL, 1.1 mmol), oxalyl chloride (0.060 mL, 0.67 mmol), alcohol **2.19** (0.19 g, 0.61 mmol), and Et_3N (0.42 mL, 3.1 mmol) were reacted to yield **2.20** (0.17 g, 91% yield, 88% *Z* as determined by quantitative ^{13}C-NMR) as a colorless oil; ^{1}H NMR ($CDCl_3$): δ 5.39 (1H, m), 5.31 (1H, m), 2.39 (2H, t, J = 7.5

Hz), 2.38 (2H, t, *J* = 7.6 Hz), 2.04 (2H, m), 1.99 (2H, m), 1.63 (2H, m), 1.56 (2H, m), 1.20-1.37 (20H, m), 0.88 (6H, m); ^{13}C NMR ($CDCl_3$): δ 211.4, 131.0, 128.7, 42.9, 42.1, 31.9, 31.5, 29.6, 29.5, 29.4 (2C), 29.3 (2C), 23.9, 22.7, 22.6, 14.1 (2C); HRMS (FAB): 309.3148, $[C_{21}H_{40}O+H]^+$ requires 309.3157.

(*Z*)-Pentadec-4-en-1-ol (2.21)

In a glovebox, a 20 mL vial was charged with 4-pentenol (410 μL, 3.98 mmol), 1-dodecene (4.4 mL), and THF (2.7 mL). A solution of **2.1** (0.025 g, 1 mol%) in THF (0.5 mL) was added, and the mixture was stirred in an open vial for 6 hours at 35 °C. The vial was removed from the glovebox, the reaction was quenched with excess ethyl vinyl ether, and the solvent was removed *in vacuo*. Flash chromatography of the residue (SiO_2, using a gradient of hexanes to 8% EtOAc in hexanes) provided **2.21** (0.56 g, 62% yield, 84% *Z* as determined by ^{13}C-NMR) as a colorless oil; ^{1}H NMR ($CDCl_3$): δ 5.38 (2H, m), 3.65 (2H, m), 1.95-2.14 (4H, m), 1.63 (2H, m), 1.52 (1H, s), 1.25 (16H, m), 0.87 (3H, t, J = 6.9 Hz); ^{13}C NMR (100 Hz, $CDCl_3$): δ 131.0, 128.9, 62.8, 32.8, 32.1, 29.9, 29.8, 29.7 (2C), 29.5 (2C), 29.3, 23.7, 22.8, 14.2; HRMS (FAB): 227.2372, $[C_{15}H_{30}O+H]^+$ requires 227.2369.

(*Z*)-Pentadecen-4-en-1-yl 4-methylbenzenesulfonate (2.22)

A 10 mL round bottom flask was charged with **2.21** (0.48 g, 2.12 mmol), Et_3N (590 μL, 4.24 mmol), 4-dimethylaminopyridine (0.03 g, 0.21 mmol), and CH_2Cl_2 (5 mL) under an argon atmosphere. The solution was cooled to 0 °C, and a solution of 4-toluenesulfonyl chloride (0.61 g, 3.18 mmol) in CH_2Cl_2 (1 mL) was added drop wise. The mixture was stirred vigorously for 4 hours at room temperature. The reaction mixture was treated with saturated aqueous $NaHCO_3$ (10 mL). After stirring at room temperature for 20 minutes, ethyl acetate (20 mL) was added. The organic layer was separated and washed with water (3x100 mL) and brine (50 mL), and dried

over $MgSO_4$. The solution was filtered and the solvent was removed *in vacuo*. Flash chromatography of the residue (SiO_2, using a gradient of 2:1 hexanes/CH_2Cl_2 to 1:1 hexanes/CH_2Cl_2) provided **2.22** (0.68 g, 84% yield, 84% *Z* as determined by ^{13}C-NMR) as a colorless oil; ^{1}H NMR ($CDCl_3$): δ 7.79 (2H, d, J=8.3 Hz), 7.33 (2H, d, J = 8.9 Hz), 5.19-5.40 (2H, m), 4.02 (2H, t, J = 6.4 Hz), 2.44 (3H, s), 1.91-2.08 (4H, m), 1.66-1.71 (2H, m), 1.25 (16H, m), 0.88 (3H, t, J = 7.0 Hz); ^{13}C NMR (100 Hz, $CDCl_3$): δ 144.8, 144.7, 133.3, 131.8, 129.9, 128.0, 127.8, 127.4, 70.2, 32.6, 32.0, 29.7 (2C), 29.6 (2C), 29.5, 29.4, 29.0, 27.3, 23.1, 22.8, 14.3; HRMS (FAB): 381.2477, $[C_{22}H_{36}O_3S+H]^+$ requires 381.2458.

***cis*-7,8-Epoxy-2-methyloctadecane ((±)-2.24)**

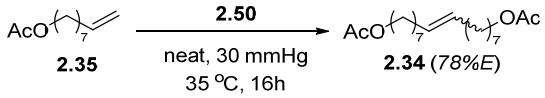
A 10 mL vial was charged with **2.22** (0.62 g, 1.63 mmol) and THF (2.2 mL) under an argon atmosphere and cooled to −78 °C. 2 M isobutylmagnesium bromide in Et_2O (1.2 mL, 2.45 mmol) was added. Next, 0.1 M Li_2CuCl_4 in THF (160 μL, 0.016 mmol) was added in one portion, and the reaction mixture was warmed to room temperature and allowed to stir overnight. An ice-cooled saturated aqueous NH_4Cl solution (5 mL) was added and the solution was extracted with pentane (3x 5 mL). The pentane extract was washed with water (10 mL) and brine (10 mL), dried over $MgSO_4$, and concentrated *in vacuo*. Flash chromatography of the reside (SiO_2, using hexanes) provided a colorless oil that was used in the next step without further purification.

The crude product was taken up in CH_2Cl_2 (12 mL) and cooled to 0 °C. A solution of mCPBA (0.35 g, 2 mmol) in CH_2Cl_2 (12 mL) was added slowly. The reaction was warmed to room temperature and stirred for 3.5 hours. A saturated aqueous $NaHCO_3$ solution (25 mL) was added and the organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash chromatography of the residue (SiO_2, using a gradient of 1% EtOAc in hexanes to 15% EtOAc in hexanes) provided **(±)-2.24** (0.30 g, 65% yield, 83% *cis*-isomer as determined by ^{1}H NMR). ^{1}H NMR ($CDCl_3$): δ 2.90 (2H, p, J = 4.2 Hz), 1.49 (9H, m), 1.26 (16H, m), 1.14-1.2 (2H, m), 0.87

(9H, m); ^{13}C NMR ($CDCl_3$): δ 57.4, 57.4, 39.1, 32.2, 32.1, 29.8, 29.7, 29.6, 29.5, 28.0 (3C), 27.5, 27.4, 26.8, 26.5, 26.2, 22.8 (2C), 14.3. HRMS (FAB): 282.2922, $[C_{19}H_{38}]^+$ requires 282.2923.

General Procedure for Time Course Experiment

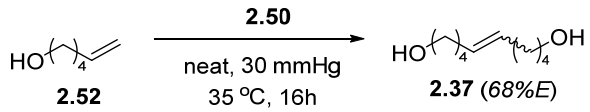
According to the procedure for compound **2.3**, oleyl alcohol (2.0 g, 7.4 mmol) and 1-hexene (8 mL) in THF (8 mL) were reacted in the presence of **2.1** (0.046 g, 1 mol%). Aliquots (1 mL) were taken at t = 0.25, 0.5, 0.75, 1, 1.5, 2, 3, 4, 5, 7, removed from the glovebox, and quenched with ethyl vinyl ether. Purification by passage through a SiO_2 plug (hexanes to CH_2Cl_2) provided a mixture of oleyl alcohol, 9-decenol, and **2.3**, which was analyzed by quantitative ^{13}C-NMR spectroscopy.



Synthesis of 2.34: Representative Procedure for synthesis of *E*-dominant symmetric internal olefin (metathesis homocoupling of terminal olefin):

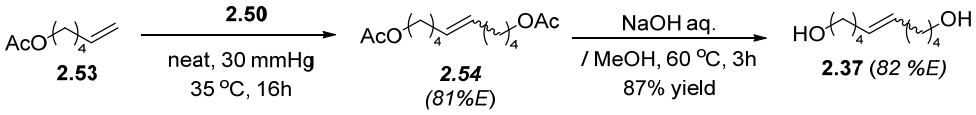
A 50 ml Schlenk flask was charged with **2.35** (4.2 g, 23 mmol) and **2.50** (190 mg, 0.23 mmol). The flask was sealed and placed on a vacuum line (Buchi Vacuum Controller B-721), and the mixture was stirred at 35˚C for 16 h under vacuum (30 mmHg). The reaction was quenched by adding tris(hydroxymethyl)phosphine (840 mg, 6.8 mmol), THF (20 ml) and water (10 ml). After stirring at 60 ˚C for 4 h, the mixture was extracted with diethyl ether and the organic solution was washed with water, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (SiO_2; *n*-hexane ~ ethyl acetate/*n*-hexane=1/20) to give pure **2.34** (2.6 g, 7.7 mmol, 68% yield, 78 %*E*) as a colorless oil. ^{1}H NMR of *E*-isomer (500 MHz, $CDCl_3$): δ 5.41-5.37 (m, 2H), 4.04 (t, *J* = 6.8 Hz, 4H), 2.04 (s, 6H), 1.98-1.94 (m, 4H), 1.66-1.55 (m, 4H), 1.43-1.19 (m, 16H). ^{1}H NMR of *Z*-isomer (500 MHz, $CDCl_3$): δ 5.35-5.30 (m,

2H), 4.04 (t, *J* = 6.8 Hz, 4H), 2.04 (s, 6H), 2.02-1.99 (m, 4H), 1.66-1.55 (m, 4H), 1.43-1.19 (m, 16H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.3, 130.4, 64.7, 32.6, 29.6, 29.2, 29.1, 28.7, 26.0, 21.1. HRMS (EI+): Calc for $C_{20}H_{36}O_4$ (M^+): 340.2614. Found: 340.2607.



Synthesis of 2.37

This compound was prepared from **2.52** (2.9 g, 29 mmol) as described in the synthesis of **2.34**. The crude product was purified by flash column chromatography (SiO_2; ethyl acetate/*n*-hexane=1/1 ~ 3/1) to give pure **2.37** (1.7 g, 9.9 mmol, 67% yield, 68 %*E*) as a colorless oil. ^{1}H NMR (500 MHz, acetone-d_6): δ 5.47-5.32 (m, 2H), 3.58-3.48 (m, 4H), 3.42 (br s, 1H), 2.86-2.82 (m, 1H), 2.09-1.95 (m, 4H), 1.58-1.33 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 130.5, 63.0, 32.4, 32.3, 25.8. HRMS (EI+): Calc for $C_{10}H_{20}O_2$ (M^+): 172.1463. Found: 172.1467.

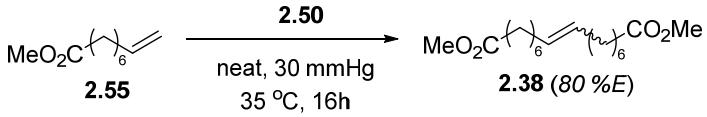


Synthesis of 2.54 and 2.37

2.54 was prepared from **2.53** (5.4 g, 38 mmol) as described in the synthesis of **2.34**. The crude product was purified by flash column chromatography (SiO_2; ethyl acetate/*n*-hexane=1/9) to give pure **2.54** (4.3 g, 17 mmol, 88% yield, 81 %*E*) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.44-5.32 (m, 2H), 4.05 (t, *J* = 6.7 Hz, 4H), 2.04 (s, 6H), 2.12-1.95 (m, 4H), 1.70-1.57 (m, 4H),

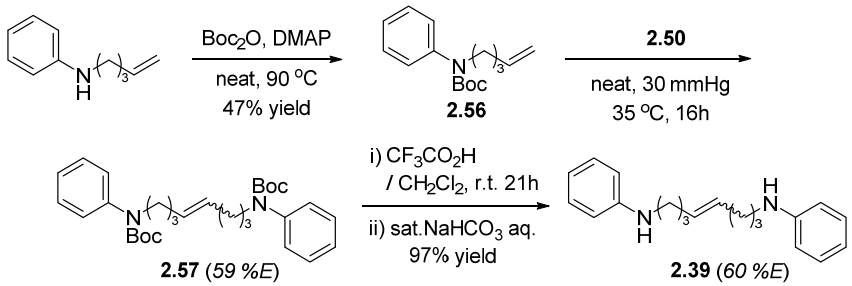
1.49-1.32 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.4, 130.4, 64.6, 32.2, 28.2, 26.0, 21.2. HRMS (EI+): Calc for $C_{14}H_{25}O_4$ ([M+H]$^+$): 257.1753. Found: 257.1745.

To a solution of **2.54** (4.3 g, 17 mmol, 81 %*E*) in methanol (50 ml) was slowly added a 10 *N* sodium hydroxide aqueous solution (50 ml). After stirring at 60 °C for 3 h, the mixture was extracted with dichloromethane and the organic solution was washed with a saturated ammonium chloride solution, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (SiO_2; ethyl acetate/*n*-hexane=1/1 ~ 3/1) to give pure **2.37** (2.5 g, 15 mmol, 87% yield, 82 %*E*) as a colorless oil.



Synthesis of 2.38

2.38 was prepared from **2.55** (3.3 g, 19 mmol) as described in the synthesis of **2.34**. The crude product was purified by flash column chromatography (SiO_2; *n*-hexane ~ ethyl acetate/*n*-hexane=1/9 ~ 1/4) to give pure **2.38** (2.7 g, 8.6 mmol, 89% yield, 80 %*E*) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.42-5.29 (m, 2H), 3.66 (s, 6H), 2.30 (t, *J* = 7.6 Hz, 4H), 2.05-1.89 (m, 4H), 1.69-1.55 (m, 4H), 1.40-1.23 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.4, 130.4, 51.6, 34.2, 32.6, 29.5, 29.1, 28.8, 25.0. HRMS (FAB+): Calc for $C_{18}H_{33}O_4$ ([M+H]$^+$): 313.2379. Found: 313.2388.



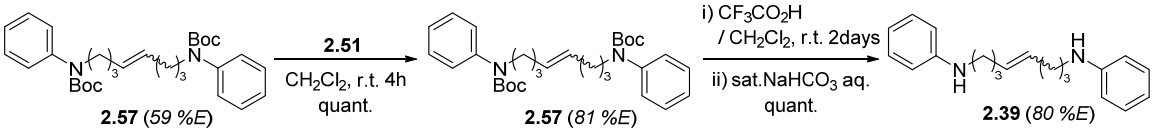
Synthesis of 2.56, 2.57, and **2.39**

N-(Pent-4-enyl)aniline (2.2 g, 14 mmol), di-*tert*-butyl dicarbonate (4.5 g, 21 mmol) and 4-(dimethylamino)pyridine (170 mg, 1.4 mmol) were combined and the mixture was stirred at 90 °C for 17 h. Di-*tert*-butyl dicarbonate (4.5 g, 21 mmol) was added to the mixture. After addition, the mixture was stirred for an additional 5 h at 90 °C and concentrated *in vacuo*. To the resulting residue was added di-*tert*-butyl dicarbonate (2.5 g, 12 mmol) and the mixture was stirred overnight at 90 °C. The mixture was concentrated *in vacuo* and then the crude product was purified by flash column chromatography (SiO_2; chloroform/*n*-hexane=1/1 ~ ethyl acetate/*n*-hexane=1/9) to give pure **2.56** (1.7 g, 6.4 mmol, 47% yield, 60 %*E*) as a red oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 8.3, 7.4 Hz, 2H), 7.23-7.14 (m, 3H), 5.77 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.03-4.88 (m, 2H), 3.68-3.58 (m, 2H), 2.09-2.00 (m, 2H), 1.64 (tt, *J* = 9.2, 6.5 Hz, 2H), 1.42 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 154.9, 142.7, 138.01, 128.9, 127.3, 126.1, 115.1, 80.2, 49.7, 31.1, 28.5, 27.8. HRMS (FAB+): Calc for $C_{16}H_{23}O_2N$ (M^+): 261.1729. Found: 261.1735.

2.57 was prepared from **2.56** (8.8 g, 33 mmol) as described in the synthesis of **2.34**. The crude product was purified by flash column chromatography (SiO_2; ethyl acetate/*n*-hexane=1/100 ~ 1/50 ~ 1/20 ~ 1/10 ~ 1/7) to give pure **2.57** (5.4 g, 11 mmol, 62% yield, 59 %*E*) as a pale yellow solid. ^{1}H NMR (500 MHz, C_6D_6): δ 7.14-7.06 (m, 8H), 7.01-6.93 (m, 2H), 5.35-5.18 (m, 2H), 3.73-3.54 (m, 4H), 1.97-1.81 (m, 4H), 1.59 (dq, *J* = 9.3, 7.5 Hz, 4H), 1.40 (s, 18H). ^{13}C NMR

(126 MHz, $CDCl_3$): δ 154.9, 142.8, 130.0, 128.8, 127.2, 126.1, 80.1, 49.8, 29.9, 28.5, 24.6. HRMS (FAB+): Calc for $C_{30}H_{42}O_4N_2$ (M^+): 494.3145. Found: 494.3165.

To a solution of **2.57** (4.0 g, 8.1 mmol, 59 %*E*) in dichloromethane (20 ml) was slowly added trifluoroacetic acid (20 ml) and the mixture was stirred for 21 h at room temperature. The reaction mixture was concentrated *in vacuo*, and chloroform and a saturated sodium bicarbonate solution was added to the resulting residue. The mixture was extracted with chloroform and the organic solution was dried over Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (SiO_2; diethyl ether/*n*-hexane=1/4) to give pure **2.39** (2.3 g, 7.9 mmol, 97% yield, 60 %*E*) as an orange oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.17 (ddd, J = 8.6, 7.4, 1.2 Hz, 4H), 6.72-6.66 (m, 2H), 6.63-6.56 (m, 4H), 5.54-5.39 (m, 2H), 3.66 (br, 2H), 3.16-3.07 (m, 4H), 2.25-2.03 (m, 4H), 1.75-1.63 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 148.5, 130.3, 129.4, 117.3, 112.9, 43.6, 30.2, 29.4. HRMS (FAB+): Calc for $C_{20}H_{27}N_2$ ([M+H]$^+$): 295.2174. Found: 295.2170.

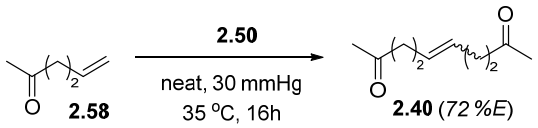


Alternative Synthesis of 2.39

To a solution of **2.57** (1.0 g, 2.0 mmol, 59 %*E*) in dichloromethane (5.0 ml) was added **2.51** (18 mg, 0.021 mmol) and the mixture was stirred for 4 h at room temperature. The reaction was quenched by adding tris(hydroxymethyl)phosphine (77 mg, 0.62 mmol), THF (20 ml) and water (20 ml). After stirring at 60 °C for 14 h, the mixture was extracted with diethyl ether and the organic solution was washed twice with water, dried over $MgSO_4$, and concentrated *in vacuo*.

The crude product **2.57** (1.1 g, quant., 81 %*E*) was used in the next step without further purification.

2.39 (80 %*E*) was prepared from **2.57** (81 %*E*) as described in the synthesis of **2.39** (60 %*E*).



Synthesis of 2.40

2.40 was prepared from **2.58** (4.0 g, 41 mmol) as described in the synthesis of **2.34**. The crude product was purified by flash column chromatography (SiO_2; ethyl acetate/*n*-hexane=1/3) to give pure **2.40** (1.2 g, 7.1 mmol, 35% yield, 72 %*E*) as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.44-5.25 (m, 2H), 2.49-2.40 (m, 4H), 2.33-2.15 (m, 4H), 2.10 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 208.4, 129.5, 43.4, 30.0, 26.7. HRMS (FAB+): Calc for $C_{10}H_{17}O_2$ ([M+H]$^+$): 169.1229. Found: 169.1235.

Representative procedure for ethenolysis at 1 atm

In a glovebox, *cis*-5-decene (19 µl, 0.10 mmol) and *trans*-5-decene (76 µl, 0.40 mmol) were combined in a 5 ml vial with a screw-cap septum top and a magnetic stir bar. A solution of the appropriate catalyst was prepared in THF. THF and the desired volume of the catalyst solution were added to the 5-decene [THF total 160 µl]. (Before adding the catalyst, an aliquot was taken for ^{1}H NMR analysis to check the *E*/*Z* ratio at the starting point.) The reaction solution was sealed, removed from the glovebox, equipped with an ethylene balloon, and then purged with ethylene before heating. After the reaction solution equipped with the ethylene balloon was allowed to stir at 35 °C for 4 h, the vial was left open to air and NMR analysis was performed.

Representative procedure for ethenolysis at 5 atm

Formation of purely *E* 5-decene (2.36): In a glovebox, *cis*-5-decene (88 mg, 120 µl, 0.63 mmol) and *trans*-5-decene (350 mg, 470 µl, 2.5 mmol) were combined in a 5 ml vial. A solution of **2.1** in THF was prepared, and the appropriate amount of THF and the catalyst solution were added to the 4:1 *E*:*Z* 5-decene mixture [THF total 972 µl and **2.1** (9.9 mg, 0.016 mmol)], and then the reaction mixture was transferred into a Fisher-Porter bottle (before adding the catalyst, an aliquot was taken for ^{1}H NMR analysis to check the *E*/*Z* ratio at the starting point). The Fisher-Porter bottle was equipped with a stir bar and the top of it was equipped with a pressure gauge. The system was sealed and taken out of the glovebox to the ethylene line. The vessel was then purged with ethylene (ultra-high purity 99.95% from Matheson Tri Gas), pressurized to 5 atm, and placed in an oil bath at 35 °C. After the reaction solution was allowed to stir for 4 h, the vessel was left open to air and the reaction solution was concentrated *in vacuo*. The crude mixture was then dissolved in hexane and loaded onto a silica gel column for purification (100% *n*-hexane as the eluting solvent). Upon concentration of the fractions containing product, 5-decene was obtained as a colorless oil (310 mg, 2.2 mmol, 72% yield, >95 %*E*).

Formation of purely *E* compound 2.12:

In a glovebox, **2.34** (1.0 g, 3.0 mmol, 78% *E*) was added to a 5 ml vial. A solution of **2.1** in THF was prepared, and the appropriate amount of THF and the catalyst solution were added to the solution [THF total 750 µl and **2.1** (9.5 mg, 0.015 mmol)], and then the reaction mixture was transferred into a Fisher-Porter bottle (before adding the catalyst, an aliquot was taken for ^{1}H NMR analysis to check the *E*/*Z* ratio at the starting point). The Fisher-Porter bottle was equipped

with a stir bar and the top of it was equipped with a pressure gauge. The system was sealed and taken out of the glovebox to the ethylene line. The vessel was then purged with ethylene (ultra-high purity 99.95% from Matheson Tri Gas), pressurized to 5 atm, and placed in an oil bath at 35 °C. After the reaction solution was allowed to stir for 4 h, the vessel was left open to air and the reaction solution was concentrated *in vacuo*. The crude mixture was then dissolved in hexane and purified by flash column chromatography (SiO_2; *n*-hexane ~ ethyl acetate/*n*-hexane=1/20). Upon concentration of the fractions containing product, **2.34** (790 mg, 2.3 mmol, 77% yield, >95 %*E*) and **2.35** (240 mg, 1.3 mmol, 21% yield) were obtained as colorless oils.

Procedure for the ethenolysis of methyl oleate:

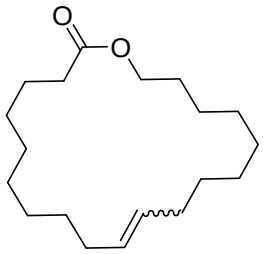
Ethenolysis reactions were carried out using research-grade methyl oleate (>99%) that was purified by storage over activated alumina followed by filtration. The experiments were set up in a glovebox under an atmosphere of argon. Methyl oleate (10 g, 34 mmol) was charged in a Fisher-Porter bottle equipped with a stir bar, pressure gauge and dip-tube adapted to the bottle. A solution of the appropriate ruthenium catalyst was prepared in dry dichloromethane, and the desired volume of this solution was added to the methyl oleate. The reaction vessel was sealed, removed from the glovebox and then attached to an ethylene line. The reaction vessel purged three times with ethylene (polymer purity 99.9% from Matheson Tri Gas), pressurized to 150 psi, and placed in an oil bath at 40 ℃. The reaction was monitored by collecting samples via the dip-tube at different routine intervals and immediately quenched by the addition of a solution of tris(hydroxymethyl)phosphine (1.0 mL, 1.0 M) in isopropanol. The samples were then heated to 60 ℃ for 1 hour, diluted with distilled water, extracted with hexanes, and analyzed by GC. The GC analyses were run using a flame ionization detector. Column: Rtx-5 from Restek, 30 m - 0.25 mm i.d. - 0.25 μm film thickness. GC and column conditions: injection temperature, 250 ℃;

detector temperature, 280 °C; oven temperature, starting temperature, 100 °C; hold time, 1 min. The ramp rate was 10 °C/min to 250 °C, hold time 12 min; carrier gas helium.

***General procedure* 1: Synthesis of *E*-enriched macrocycles**

A solution of diene (1 equiv, 1.8 mmol) and benzylidene-bis(tricyclohexylphosphine)dichlororuthenium (0.074 g, 0.090 mmol) in CH_2Cl_2 (6 mM, 300 mL) was refluxed for six hours, then quenched with ethyl vinyl ether, and concentrated. Flash chromatography of the residue (SiO_2, using 2% Et_2O in pentanes for compounds **2.41** and **2.42**, 10% Et_2O in pentanes for compound **2.43**, and 66% Et_2O in pentanes for compound **2.44**) provided the product.

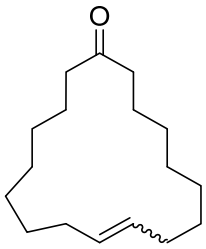
***E*-Oxacycloicos-11-en-2-one (2.41)**



(*E*)-2.41

According to *General Procedure 1* diene **2.41a** provided (***E***)-**2.41** (0.31 g, 58% yield, 69% *E* as determined by quantitative ^{13}C-NMR) as a colorless oil; ^{1}H NMR δ 5.32 (m, 2H), 4.09 (t, *J* = 5.6 Hz, 2H), 2.31 (t, *J* = 6.7 Hz, 2H), 2.01 (m, 4H), 1.63 (m, 4H), 1.26-1.41 (m, 20H); ^{13}C NMR δ 174.2, 130.8, 130.8, 64.4, 34.2, 32.0, 31.9, 29.4, 29.2, 28.9 (2C), 28.8 (2C), 28.7, 28.3, 27.7, 27.6, 26.2, 25.1.

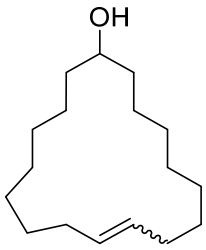
***E*-Cycloheptadec-9-enone (2.42)**



(*E*)-2.42

According to *General Procedure 1*, diene **2.42a** provided (***E***)**-2.42** (0.20 g, 44% yield, 80% *E* as determined by ^{1}H-NMR) as a colorless solid; ^{1}H NMR δ 5.31 (m, 2H), 2.37 (t, *J* = 7.1 Hz, 4H), 2.01 (m, 4H) 1.60 (m, 4H), 1.22-1.37 (m, 16H); ^{13}C NMR δ 213.4, 131.2 (2C), 42.6 (2C), 32.1 (2C), 29.0 (2C), 28.9 (2C), 28.5 (2C), 27.6 (2C), 24.2 (2C).

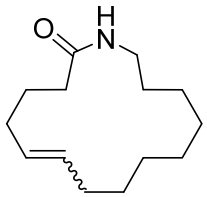
***E*-Cycloheptadec-9-enol (2.43)**



(*E*)-2.43

According to *General Procedure 1*, diene **2.43a** provided (***E***)**- 2.43** (0.18 g, 40% yield, 80% *E* as determined by quantitative ^{13}C-NMR) as a colorless solid; ^{1}H NMR δ 5.34 (m, 2H), 3.71 (m, 1H), 2.02 (m, 4H), 1.50 (m, 4H), 1.23-1.36 (m, 20H); ^{13}C NMR δ 131.0 (2C), 71.4, 35.6 (2C), 32.4 (2C), 29.2 (2C), 28.7 (2C), 28.2 (2C), 27.4 (2C), 22.9 (2C).

***E*-Azacyclopentadec-6-en-2-one (2.44)**



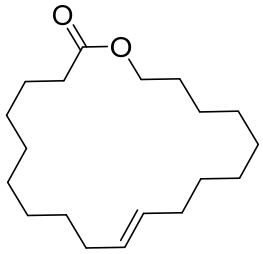
(*E*)-2.44

Similar to *General Procedure 1*, except after 6 hours a second aliquot of 5 mol% bis(tricyclohexylphosphine)benzylidine ruthenium(IV) was added and the solution refluxed for an additional 6 hours, diene **2.44a** provided (***E*)-2.44** (0.13 g, 33% yield, 55% *E* as determined by ^{1}H-NMR) as a colorless solid. ^{1}H NMR δ 5.36 (m, 2H), 5.32 (1H, *overlapped*), 3.27 (q, *J* = 5.7 Hz, 2H), 2.21 (t, *J* = 6.3 Hz, 2H), 2.13 (m, 2H), 2.01 (m, 2H), 1.78 (m, 2H), 1.45 (m, 2H), 1.34 (m, 8H), 1.26 (m, 2H); ^{13}C NMR δ 172.9, 130.4, 130.1, 38.9, 34.6, 31.5 (2C), 27.8, 27.6, 26.4, 26.2, 25.2, 23.8, 23.4.

***General procedure* 2: *Z*-selective ethenolysis of *E*-dominant macrocycles**

A solution of *E*-enriched macrocycle (1 equiv.) in THF (1M) was prepared in a 4 mL vial in a glovebox and sealed with a septum cap. Catalyst **2.1** (2 mol %) was added as a solution in a minimal amount of THF. The sealed vial was removed from the glovebox and stirred under an ethylene atmosphere. The reaction was heated (35 °C for **2.41** and **2.43**, 40 °C for **2.44**, 75 °C for **2.42**) for 2 hours, then quenched with ethyl vinyl ether and concentrated. Flash chromatography of the residue (SiO_2, using 2% Et_2O in pentanes for compounds **2.41** and **2.42**, 10% Et_2O in pentanes for compound **2.43**, and 66% Et_2O in pentanes for compound **2.44**) provided the product as the pure *E*-isomer. Isolated yields of the pure *E*-macrocycles and recovered diene were calculated based on the assumption that only the *Z*-isomer underwent ethenolysis and that it reacted completely.

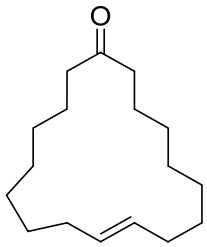
***E*-Oxacycloicos-11-en-2-one (2.41)**



(*E*)-2.41

According to *General Procedure 2* macrocycle **2.41** (97 mg, 0.33 mmol, 69% *E*) was reacted with **2.1** (4.2 mg, 7.0 μmol) and provided the pure *E*-isomer of **2.41** (47 mg, 69% yield) and diene **2.41a** (27 mg, 81% yield) as colorless oils; ^{1}H NMR δ 5.32 (m, 2H), 4.09 (t, *J* = 5.6 Hz, 2H), 2.31 (t, *J* = 6.7 Hz, 2H), 2.01 (m, 4H), 1.63 (m, 4H), 1.26-1.41 (m, 20H); ^{13}C NMR δ 174.2, 130.8, 130.8, 64.4, 34.2, 32.0, 31.9, 29.4, 29.2, 28.9 (2C), 28.8 (2C), 28.7, 28.3, 27.7, 27.6, 26.2, 25.1. HRMS (EI) 294.2549, $[C_{19}H_{34}O_2]^+$ requires 294.2559.

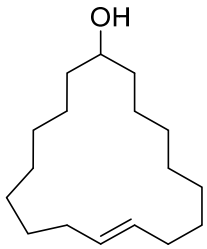
***E*-Cycloheptadec-9-enone (2.42)**



(*E*)-2.42

According to *General Procedure 2,* macrocycle **2.42** (156 mg, 0.62 mmol, 80% *E*) was reacted with **2.1** (7.9 mg, 12 μmol) and provided the pure *E*-isomer of **2.42** (50 mg, 40% yield) and diene **2.42a** (16 mg, 46% yield) as colorless solids; ^{1}H NMR δ 5.31 (m, 2H), 2.37 (t, *J* = 7.1 Hz, 4H), 2.01 (m, 4H) 1.60 (m, 4H), 1.22-1.37 (m, 16H); ^{13}C NMR δ 213.4, 131.2, 42.6, 32.1, 29.0, 28.9, 28.5, 27.6, 24.2. HRMS (FAB) 251.2372, $[C_{17}H_{30}O+H]^+$ requires 251.2375.

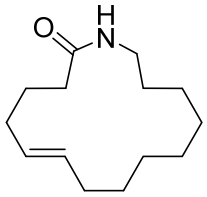
***E*-Cycloheptadec-9-enol (2.43)**



(*E*)-2.43

According to *General Procedure 2*, macrocycle **2.43** (108 mg, 0.43 mmol, 80% *E*) was reacted with **2.1** (5.4 mg, 9.0 μmol) and provided the pure *E*-isomer of **2.43** (68 mg, 78% yield) and diene **2.43a** (19 mg, 79% yield) as colorless solids; ^{1}H NMR δ 5.34 (m, 2H), 3.71 (m, 1H), 2.02 (m, 4H), 1.50 (m, 4H), 1.23-1.36 (m, 20H); ^{13}C NMR δ 131.0 (2C), 71.4, 35.6 (2C), 32.4 (2C), 29.2 (2C), 28.7 (2C), 28.2 (2C), 27.4 (2C), 22.9 (2C). HRMS (FAB) 251.2371, $[C_{17}H_{32}O_2$-H$]^+$ requires 251.2375.

***E*-A*zacyclopentadec-6-en-2-one (2.44)**



(*E*)-2.44

According to *General Procedure 2*, macrocycle **2.44** (51 mg, 0.22 mmol, 55% *E*) was reacted with **2.1** (2.8 mg, 4.4 μmol) and provided the pure *E*-isomer of **2.44** (21 mg, 75% yield) as a colorless solid, and diene **2.44a** (21 mg, 86% yield) as a pale yellow oil; ^{1}H NMR δ 5.36 (m, 2H), 5.32 (1H, *overlapped*), 3.27 (q, *J* = 5.7 Hz, 2H), 2.21 (t, *J* = 6.3 Hz, 2H), 2.13 (m, 2H), 2.01 (m, 2H), 1.78 (m, 2H), 1.45 (m, 2H), 1.34 (m, 8H), 1.26 (m, 2H); ^{13}C NMR δ 172.9, 130.4, 130.1, 38.9, 34.6, 31.5 (2C), 27.8, 27.6, 26.4, 26.2, 25.2, 23.8, 23.4. HRMS (FAB) 224.2014, $[C_{14}H_{25}NO$+H$]^+$ requires 224.2014.

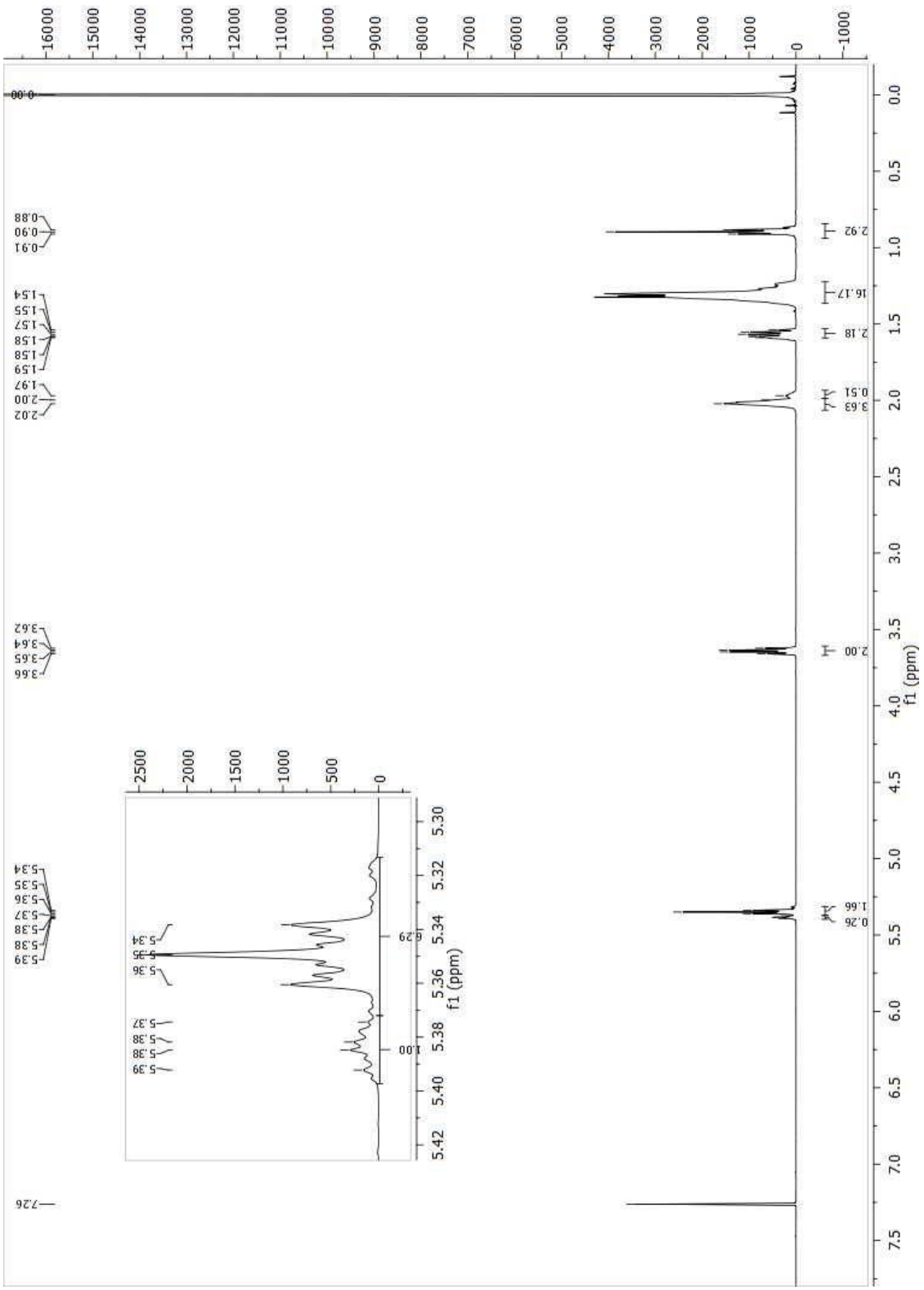


Figure 6: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (*Z*)-tetradec-9-en-1-ol (**2.3**).

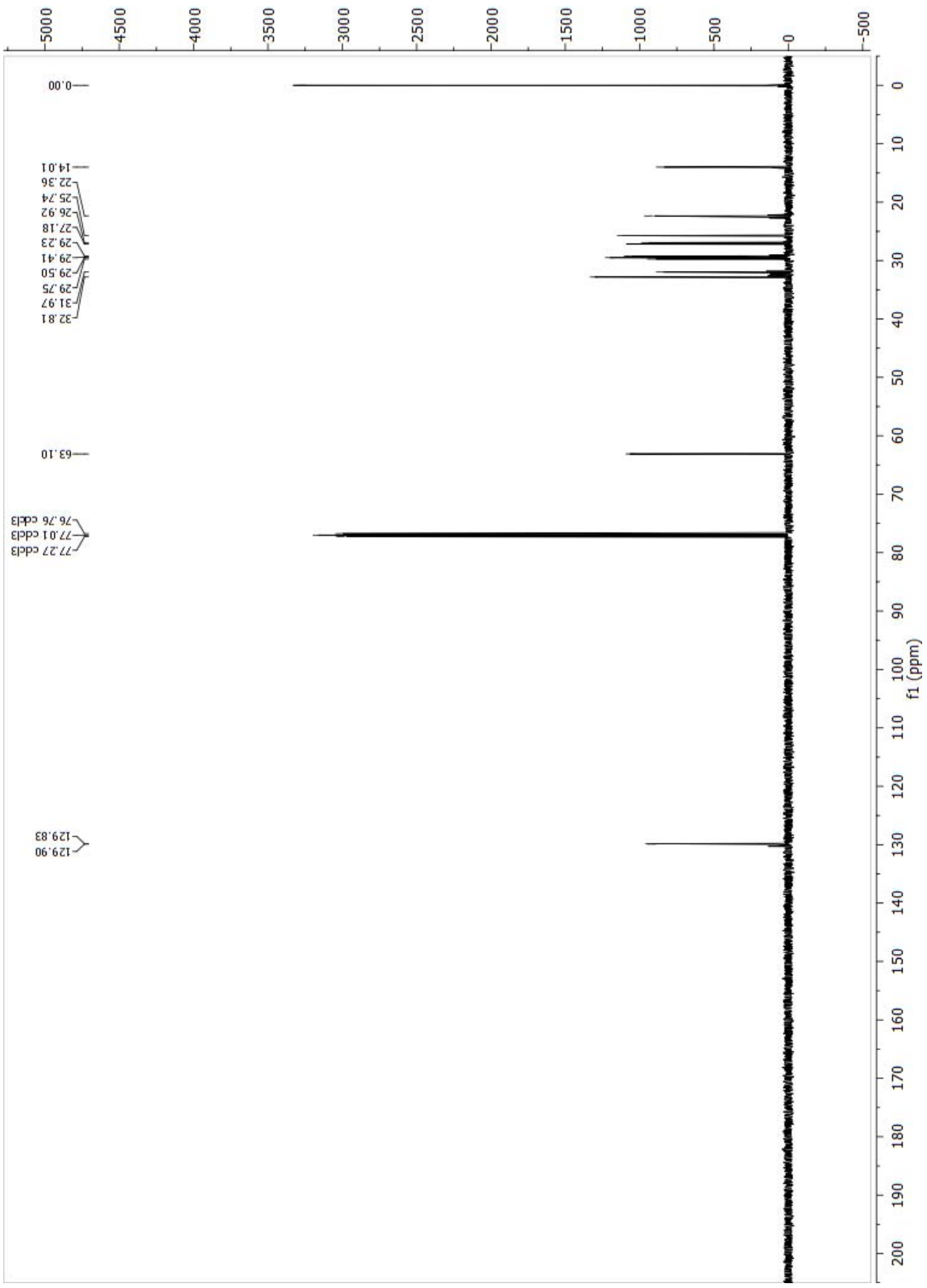


Figure 7: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (*Z*)-tetradec-9-en-1-ol (**2.3**).

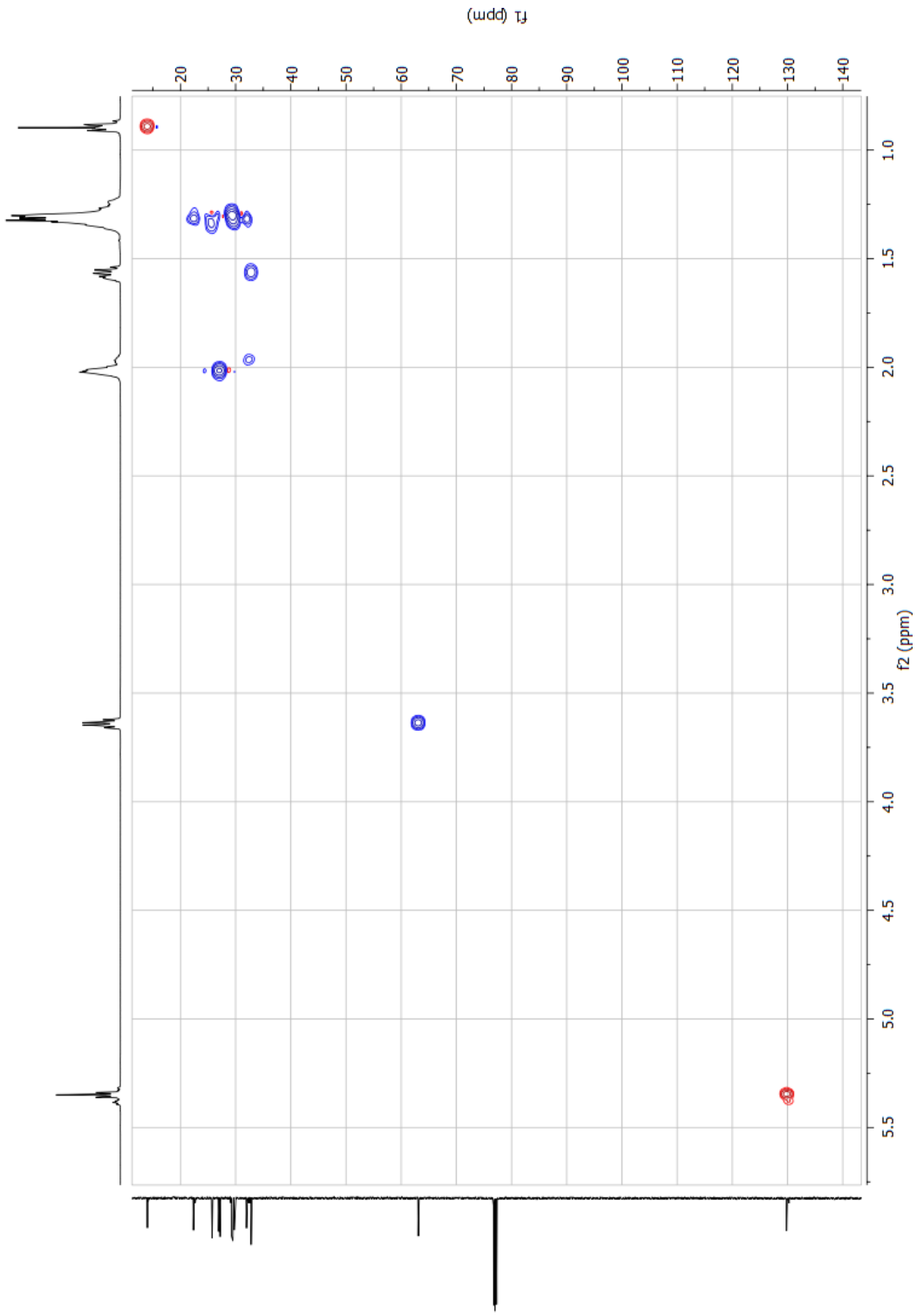


Figure 8: HSQC spectrum of (*Z*)-tetradec-9-en-1-ol (**2.3**).

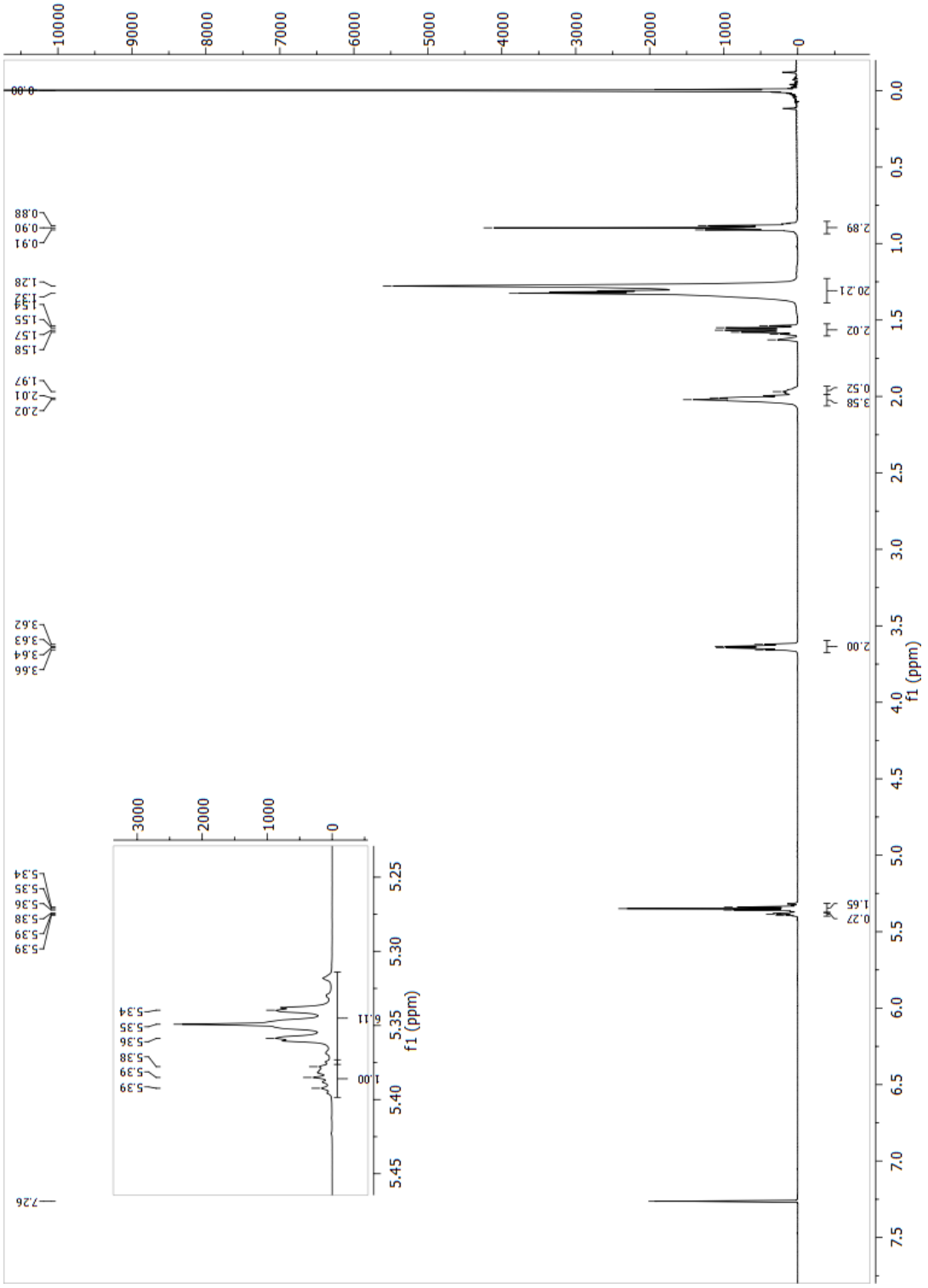


Figure 9: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (*Z*)-hexadec-11-en-1-ol (**2.5**)

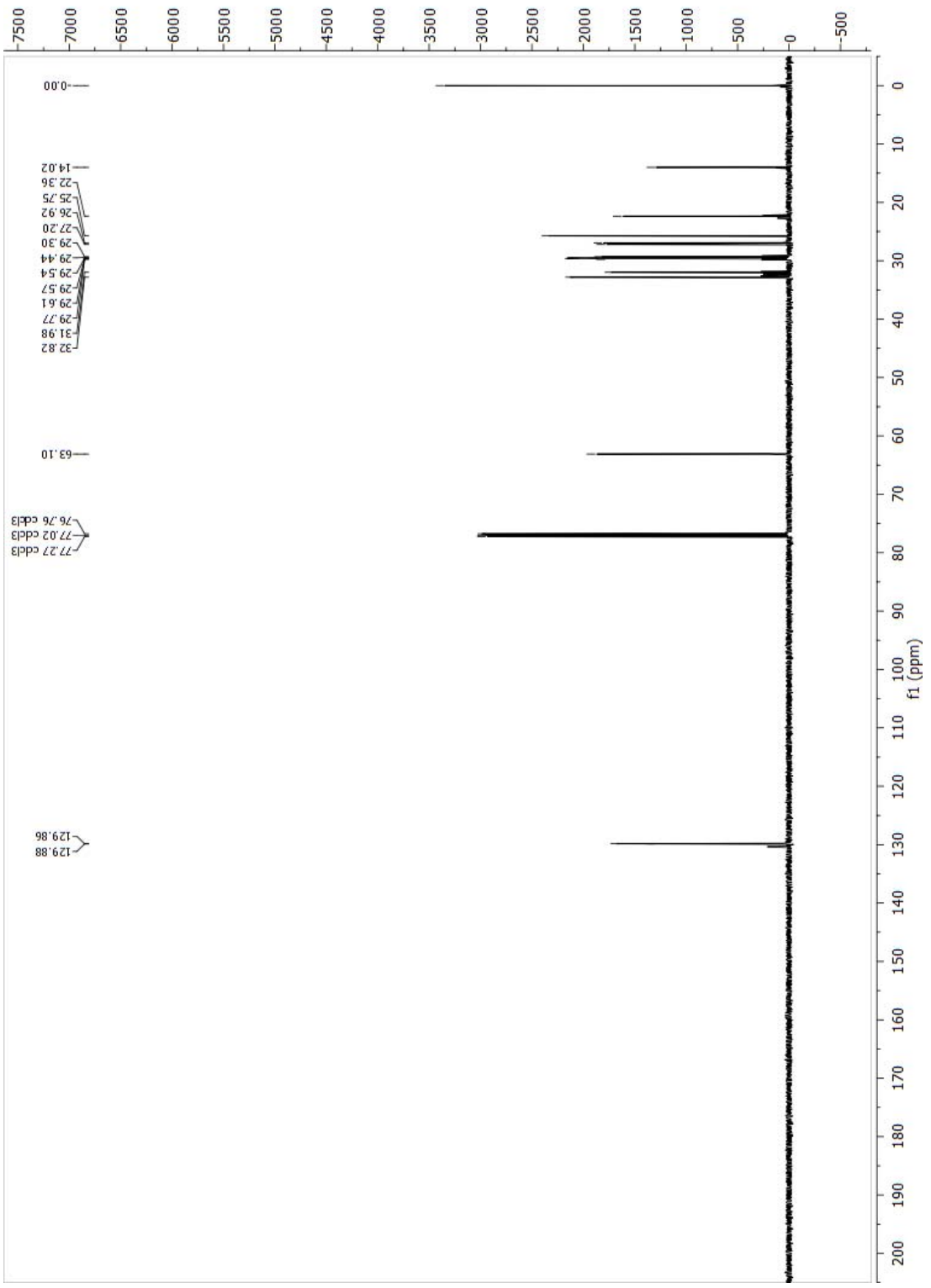


Figure 10: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (*Z*)-hexadec-11-en-1-ol (**2.5**).

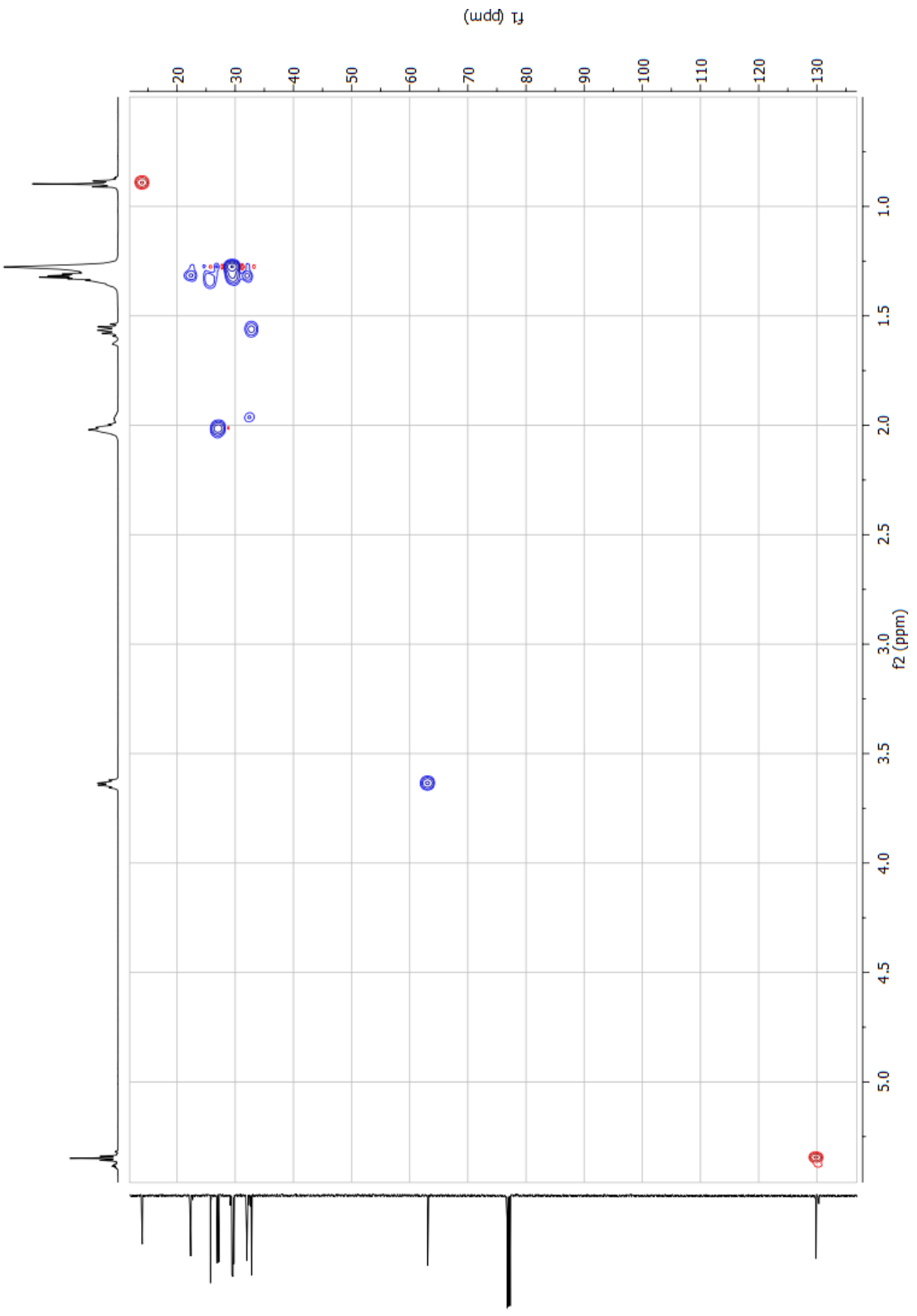


Figure 11: HSQC spectrum of (*Z*)-hexadec-11-en-1-ol (**2.5**).

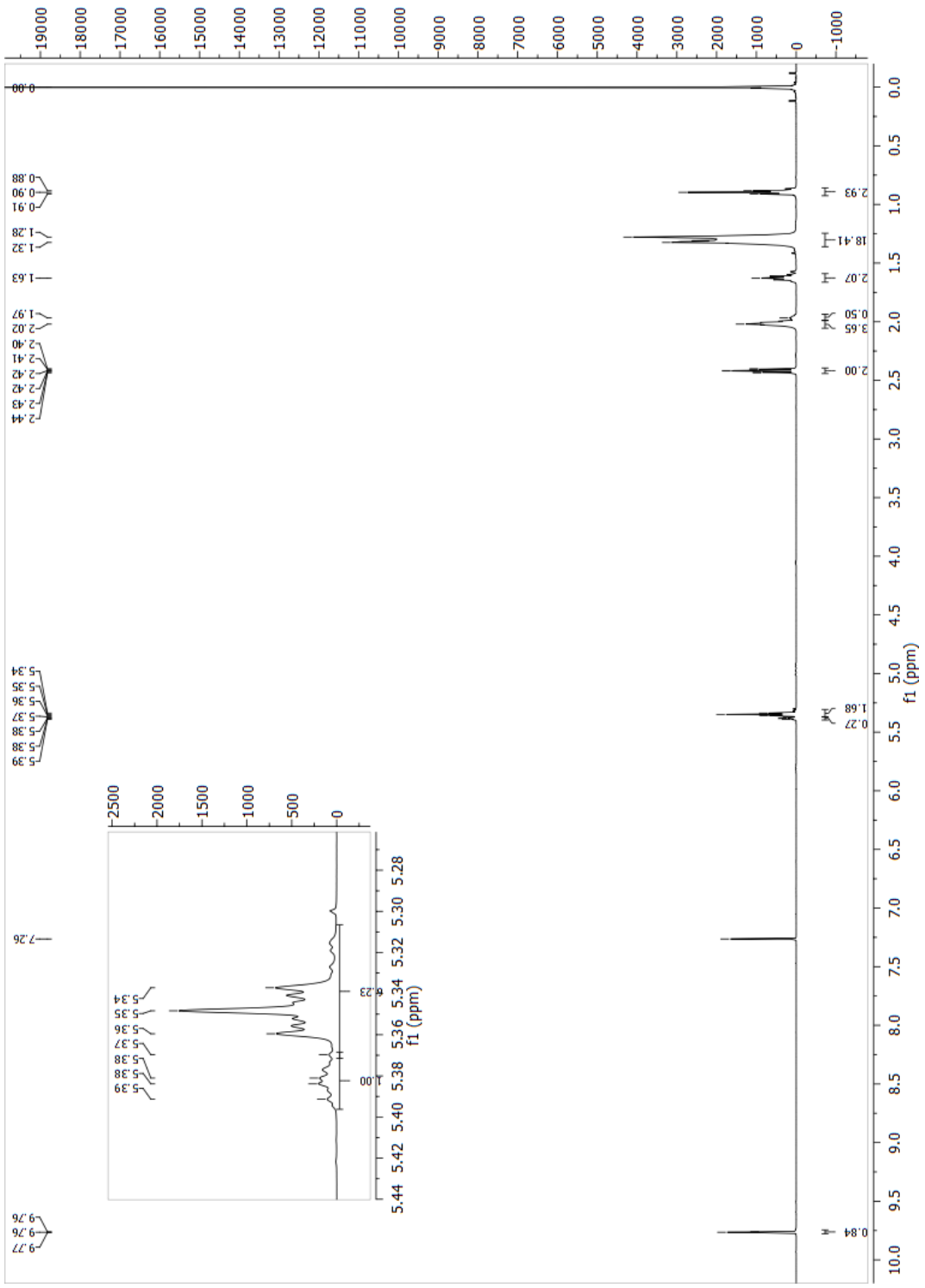


Figure 12: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (*Z*)-hexadec-11-enal (**2.6**).

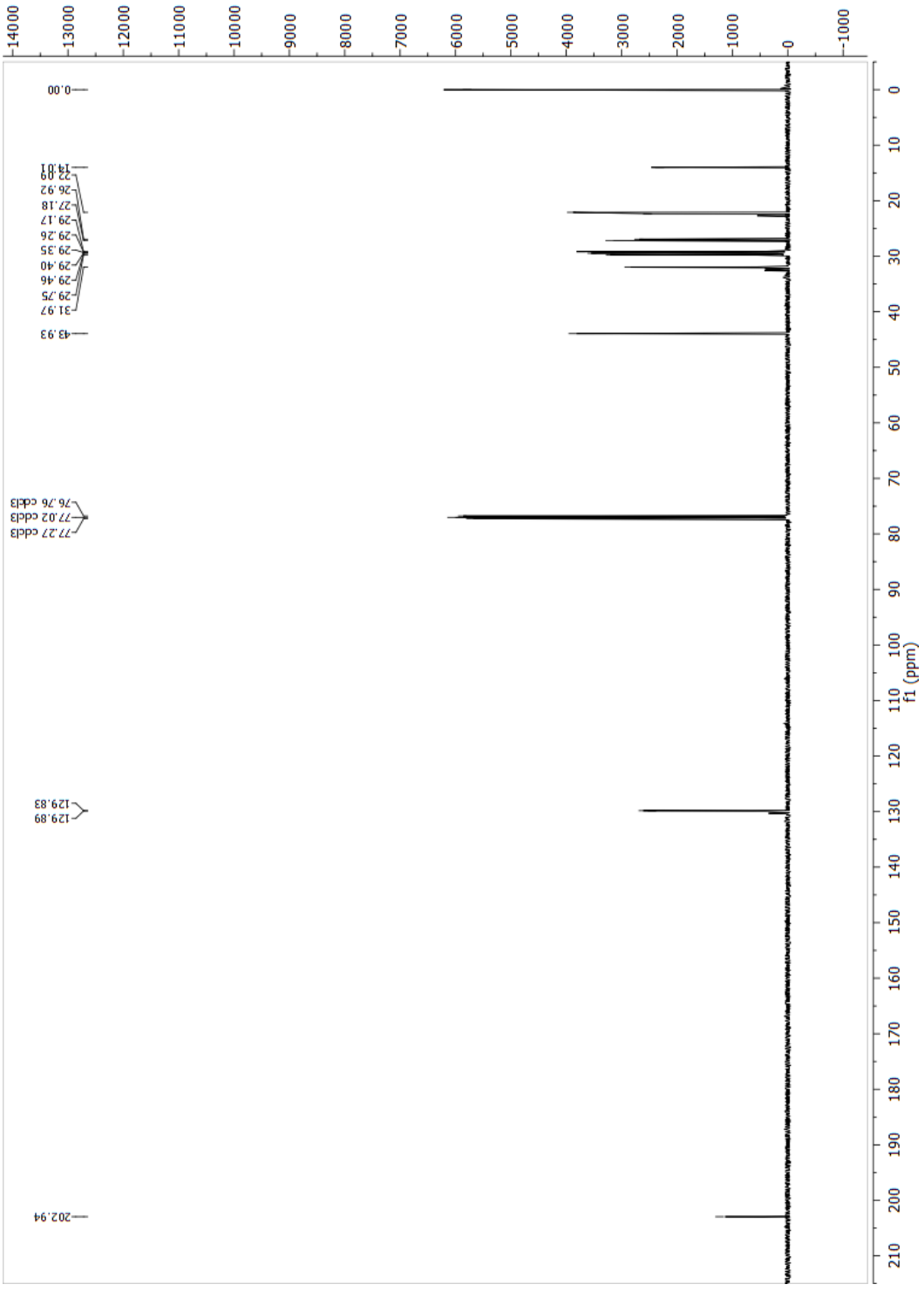


Figure 13: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (*Z*)-hexadec-11-enal (**2.6**).

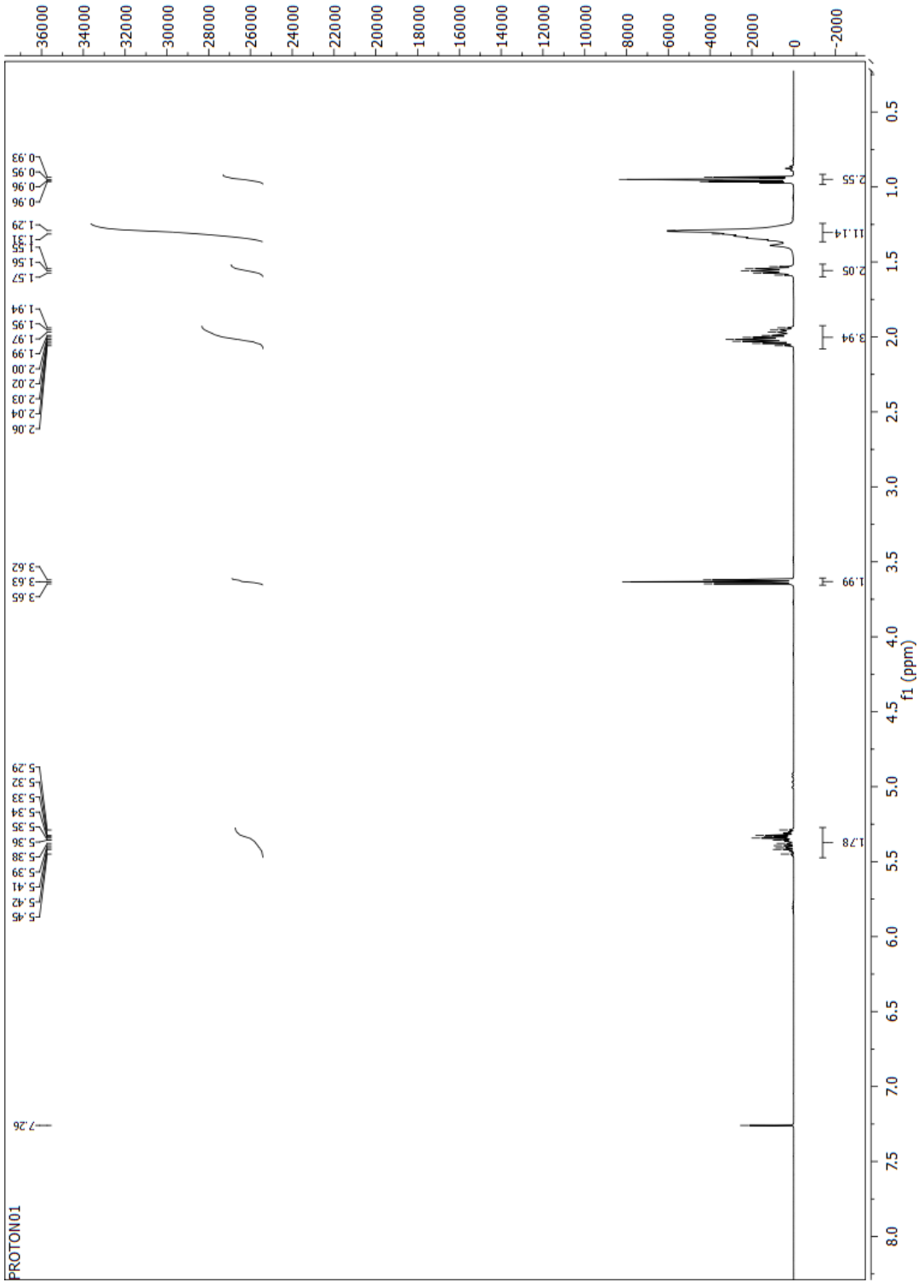


Figure 14: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (*Z*)-Dodec-9-en-1-ol (**2.7**).

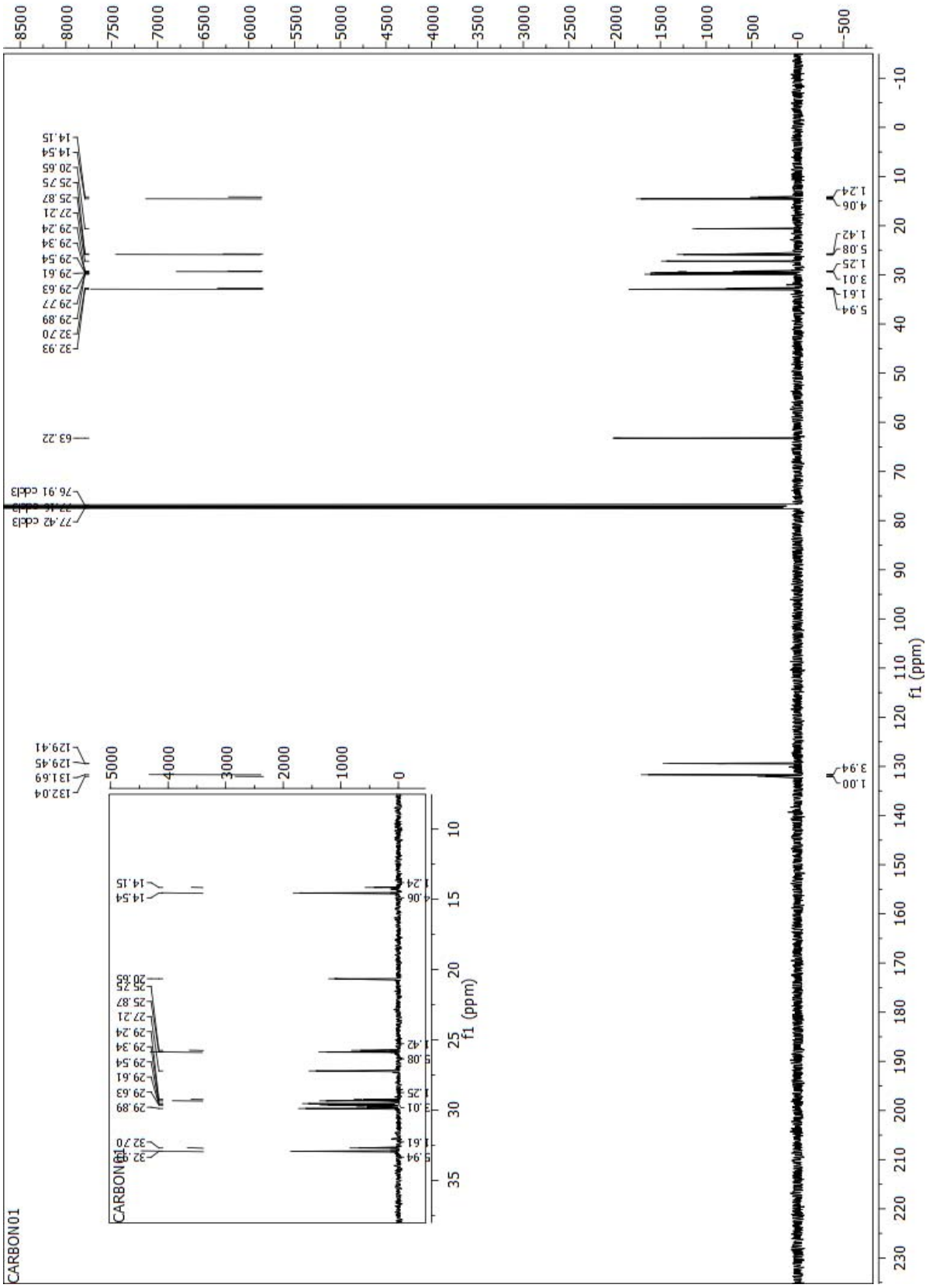


Figure 15: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (*Z*)-Dodec-9-en-1-ol (**2.7**).

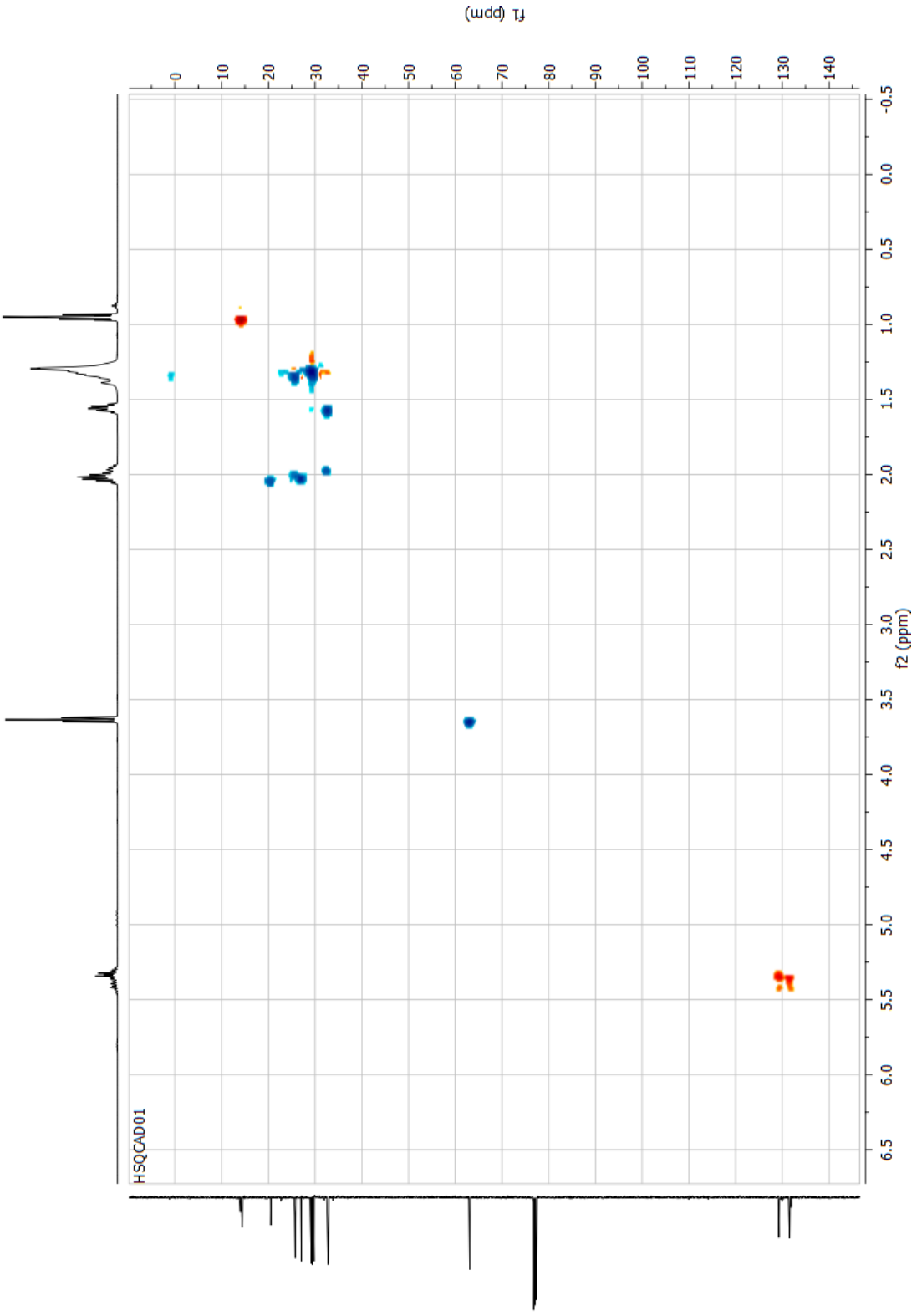


Figure 16: HSQC spectrum of (*Z*)-Dodec-9-en-1-ol (**2.7**).

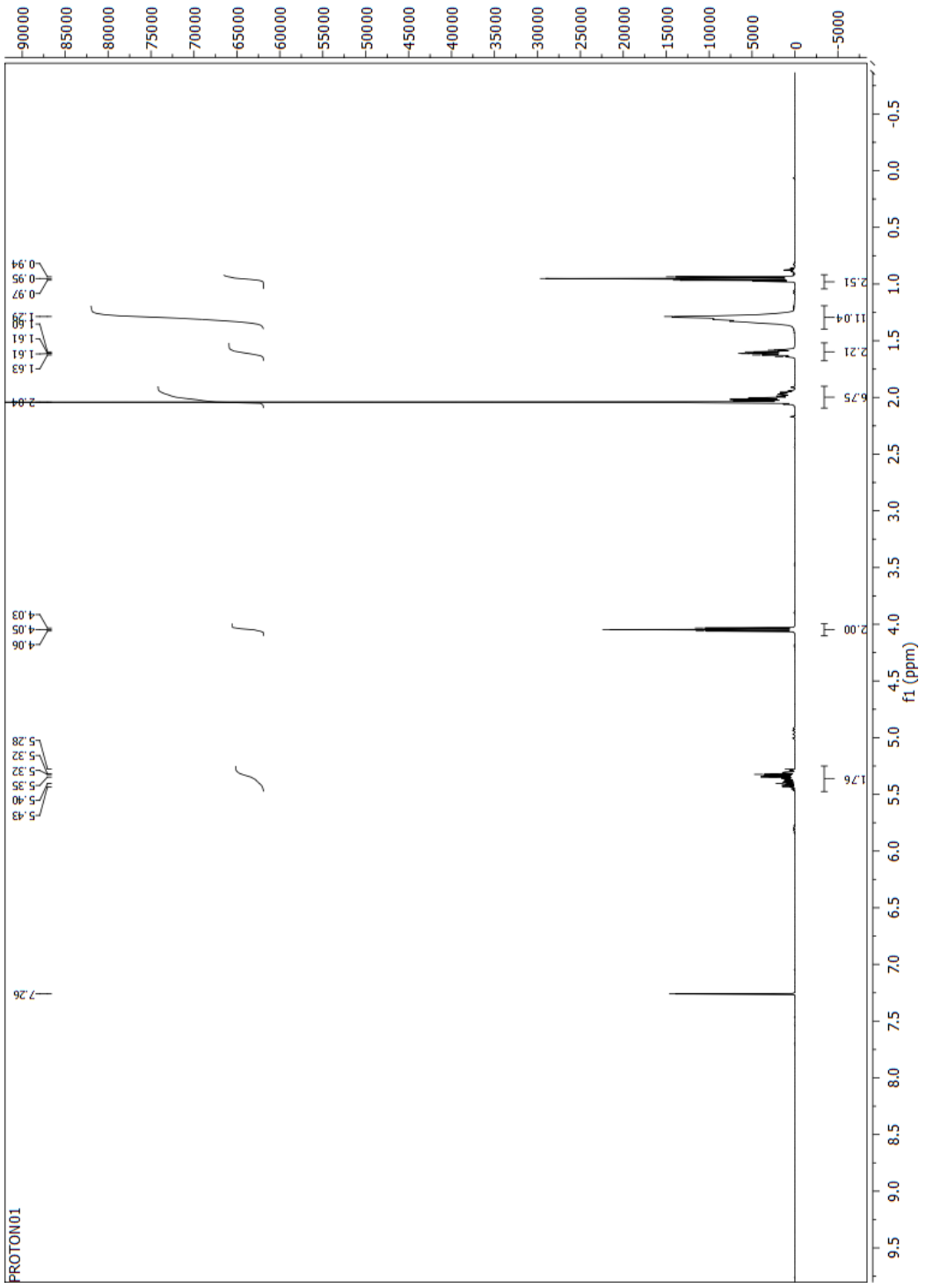


Figure 17: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (Z)-Dodec-9-en-1-yl acetate (**2.8**).

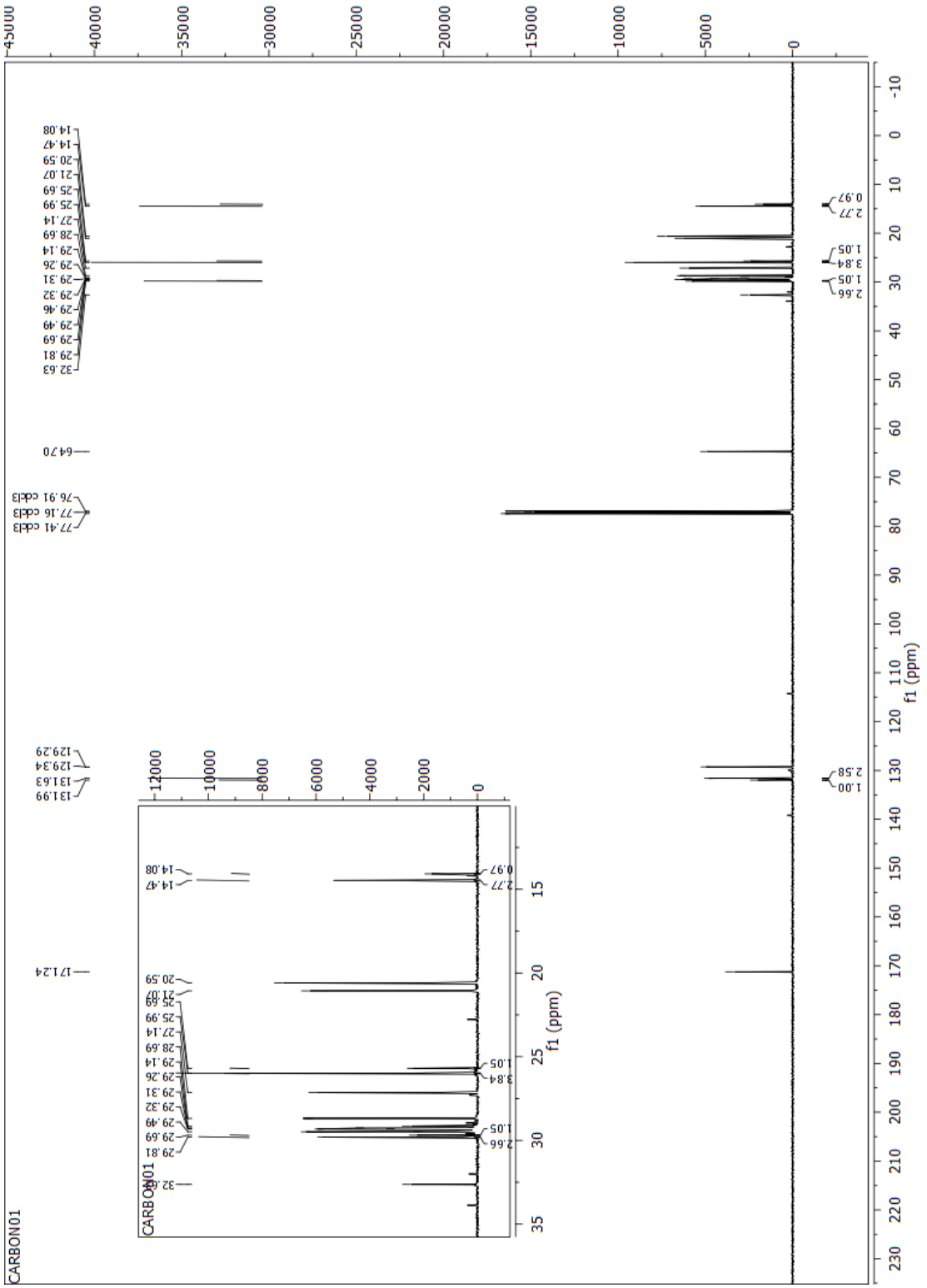


Figure 18: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (Z)-Dodec-9-en-1-yl acetate (**2.8**).

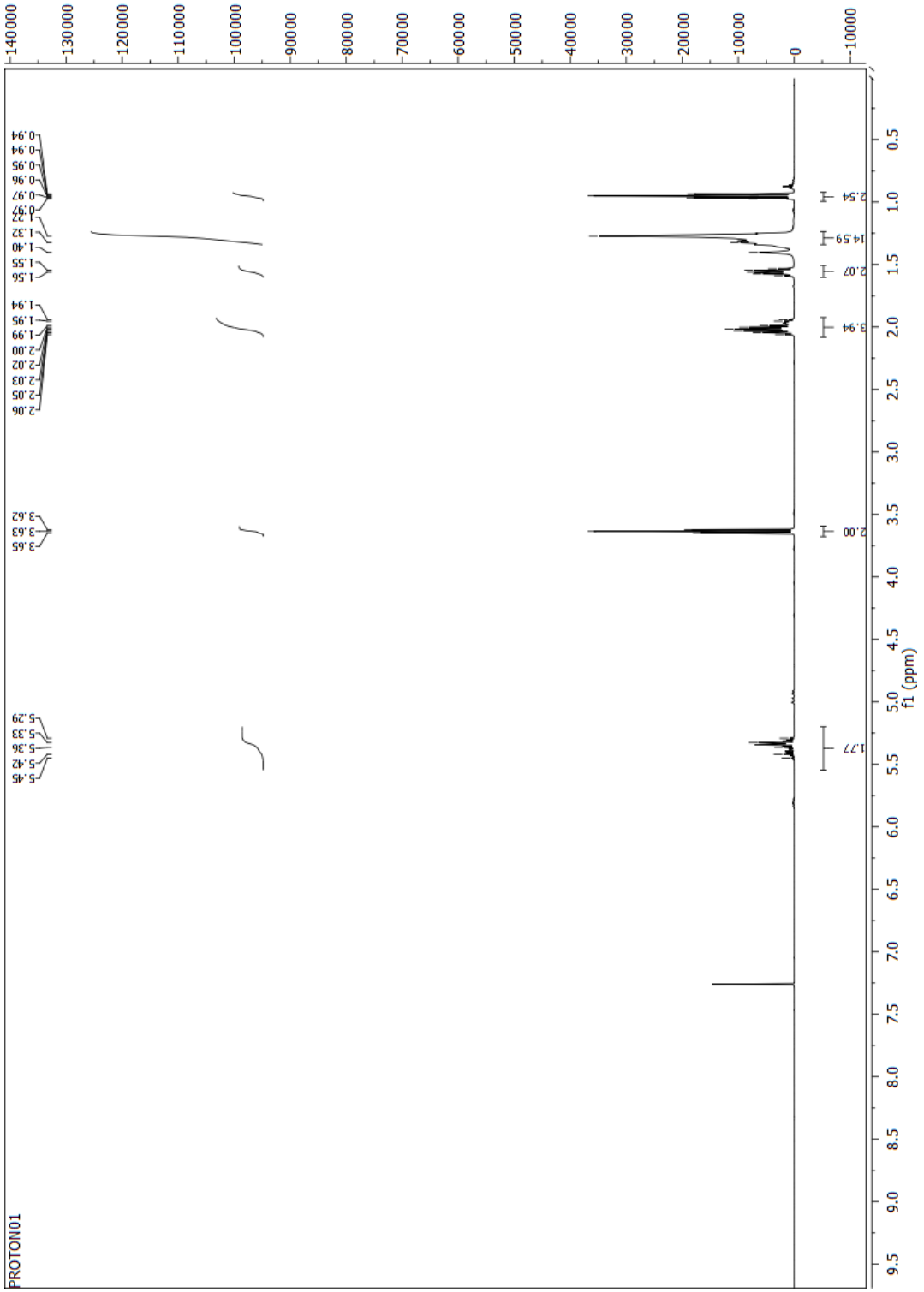


Figure 19: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (*Z*)-Tetradec-11-en-1-ol (**2.9**).

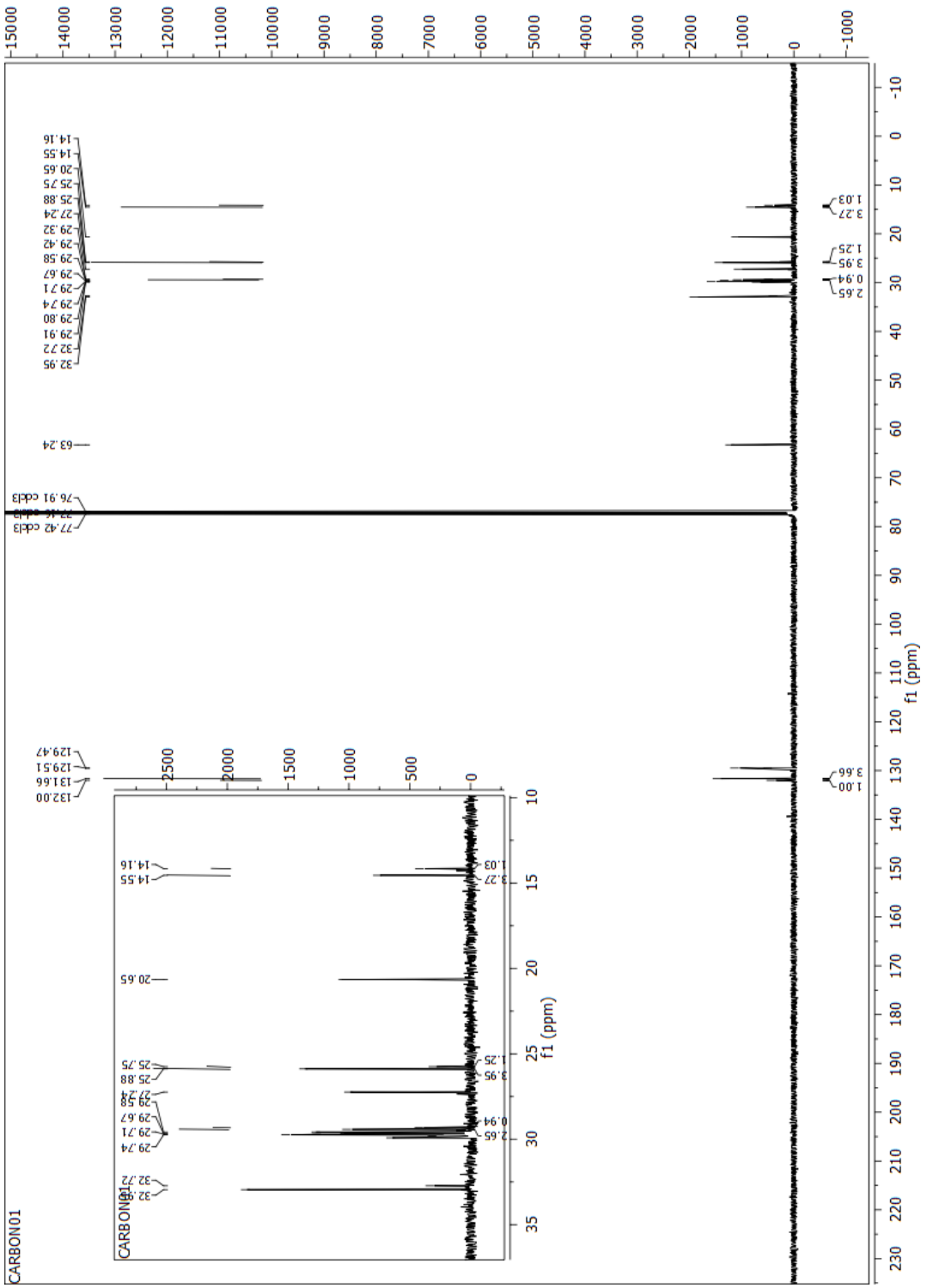


Figure 20: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (*Z*)-Tetradec-11-en-1-ol (**2.9**).

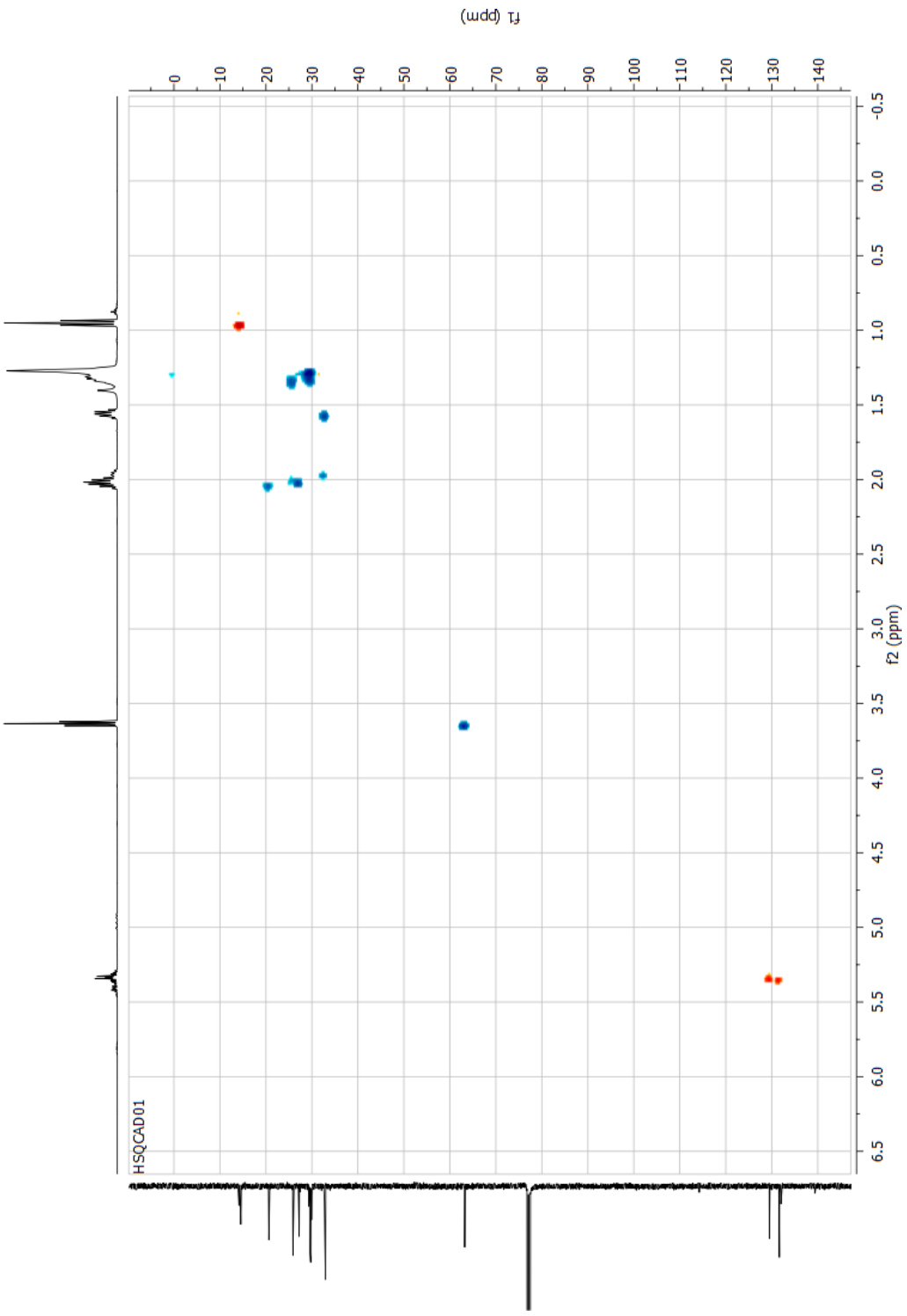


Figure 21: HSQC spectrum of (*Z*)-Tetradec-11-en-1-ol (**2.9**).

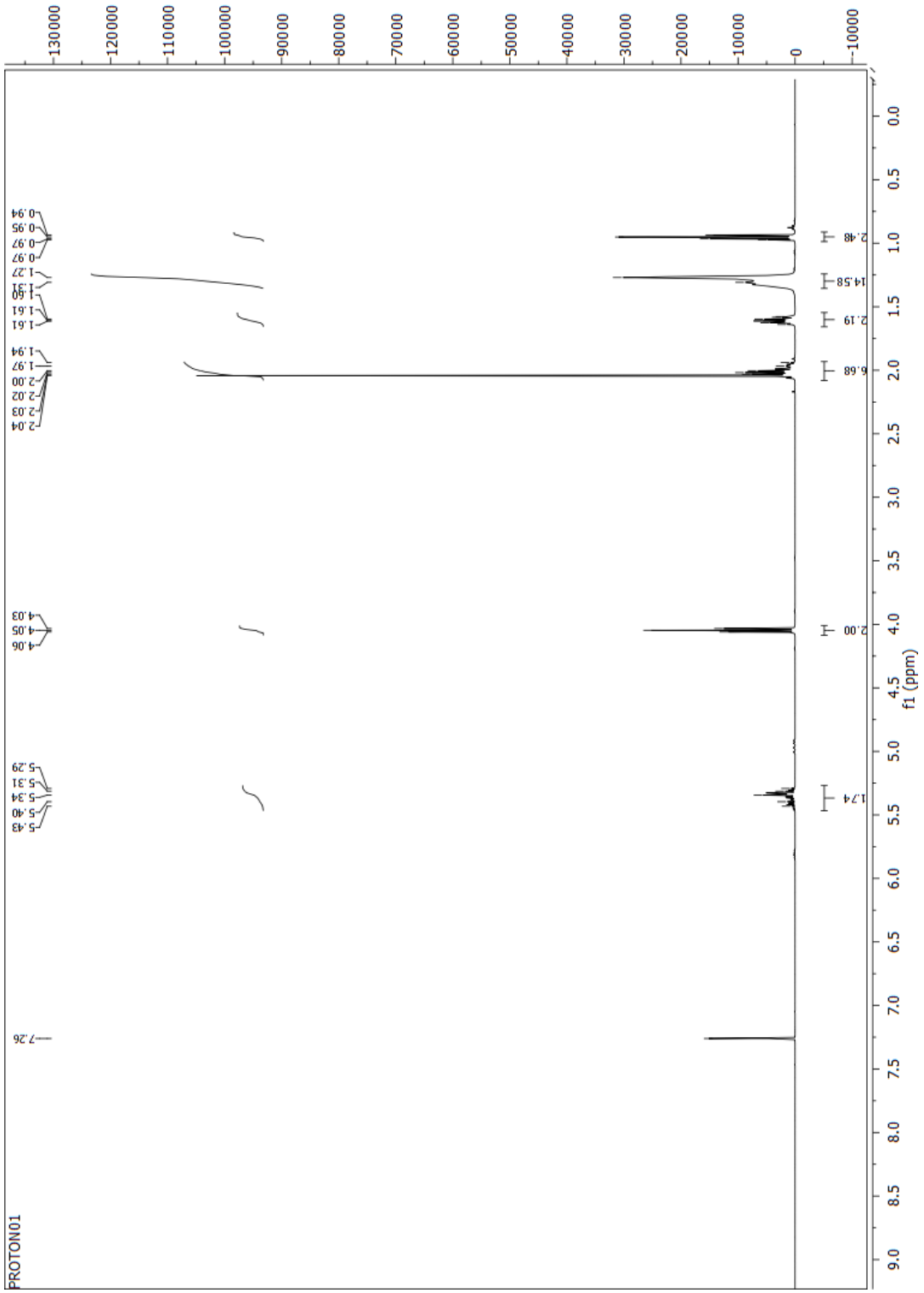


Figure 22: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (Z)-Tetradec-11-en-1-yl acetate (**2.10**).

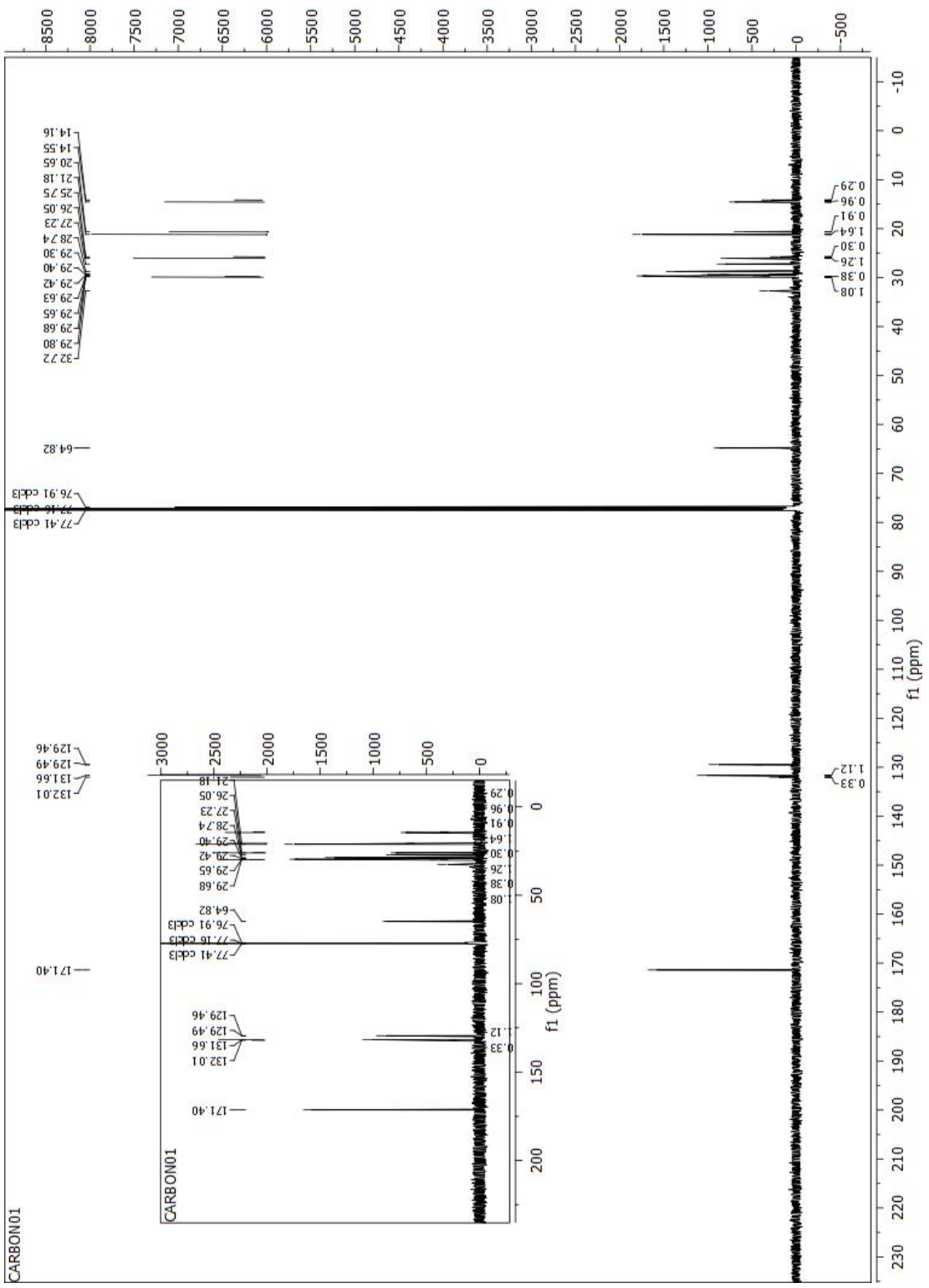


Figure 23: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (Z)-Tetradec-11-en-1-yl acetate (**2.10**).

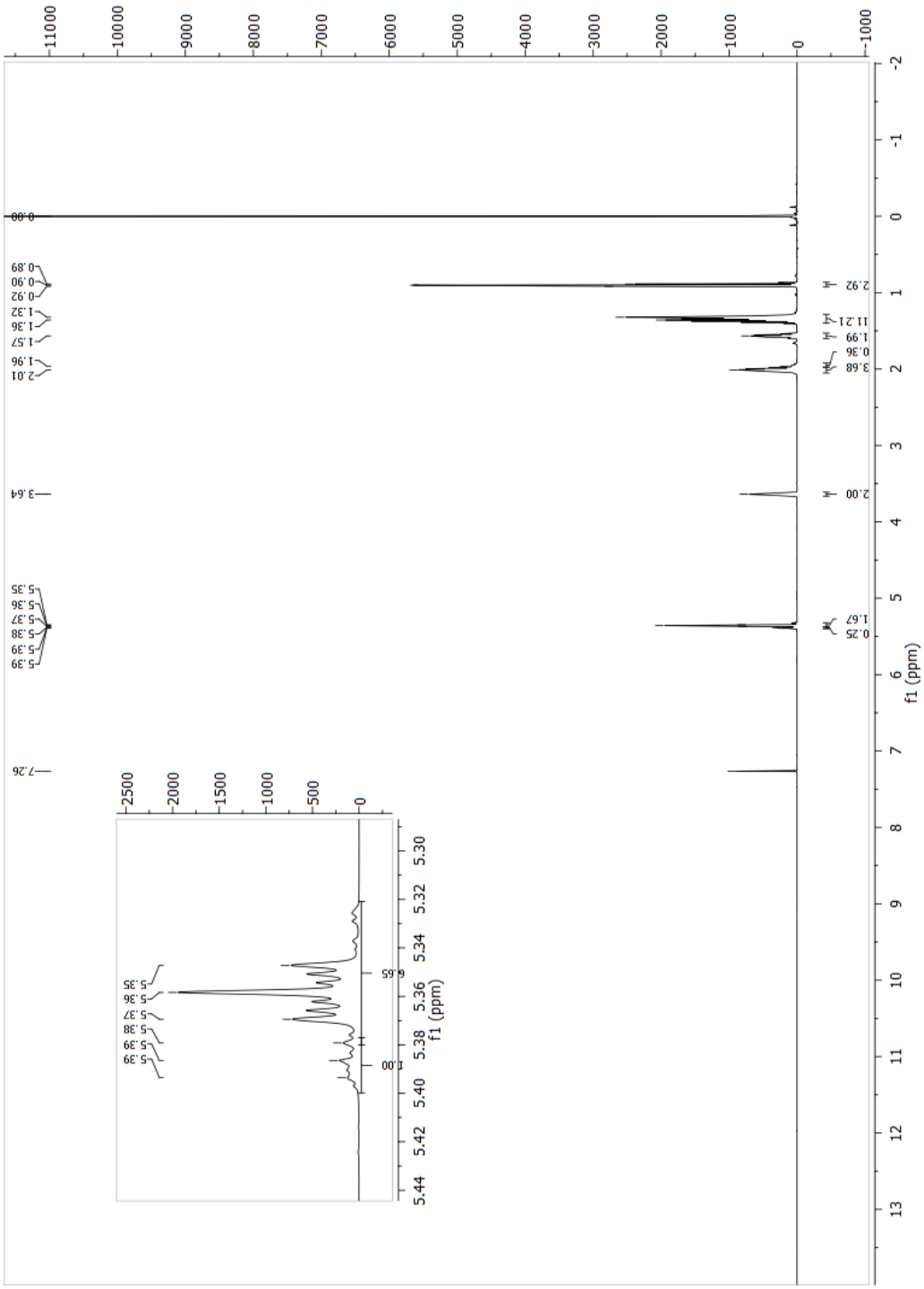


Figure 24: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (*Z*)-dodec-8-en-1-ol (**2.12**).

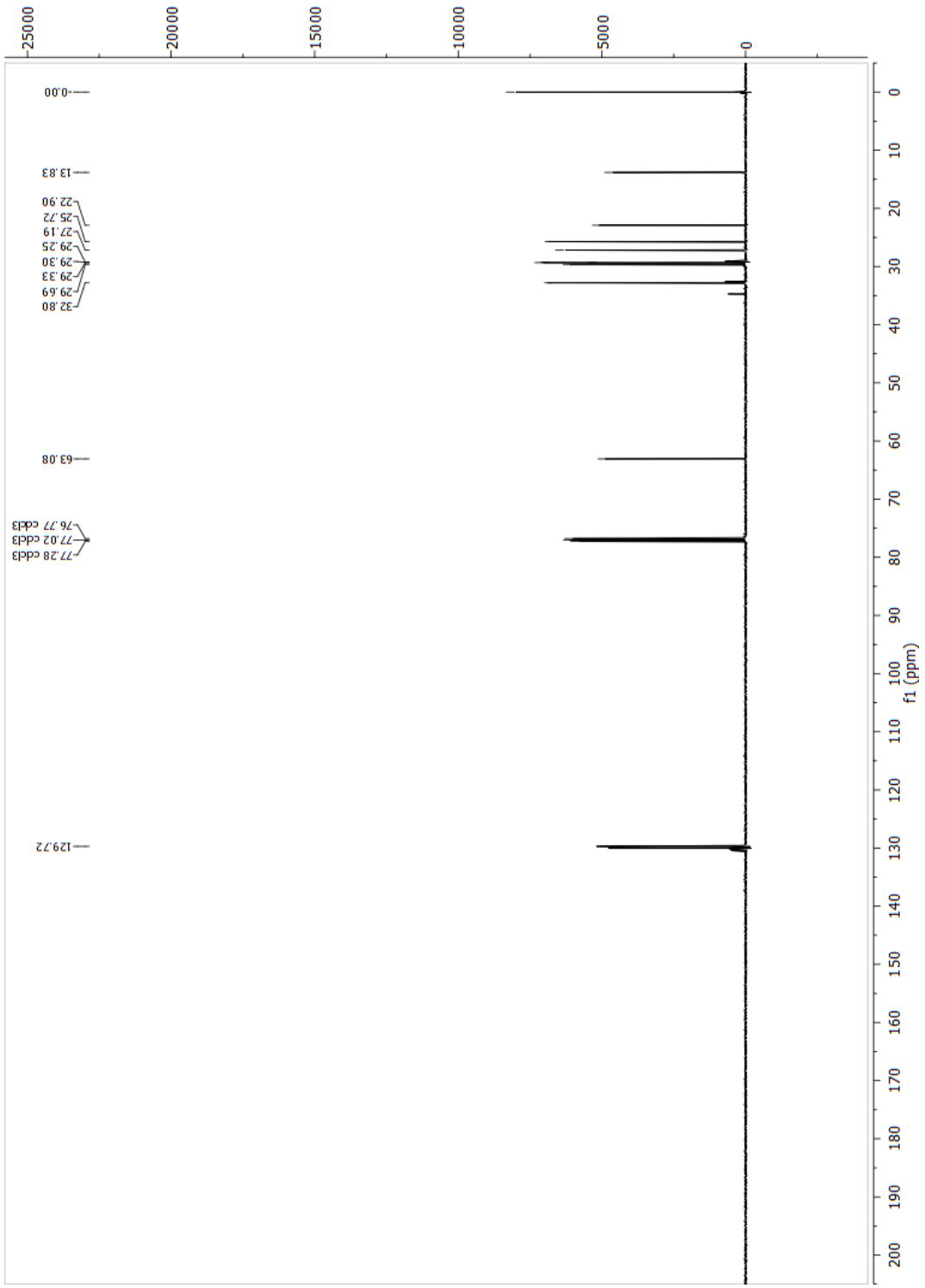


Figure 25: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (*Z*)- dodec-8-en-1-ol (**2.12**).

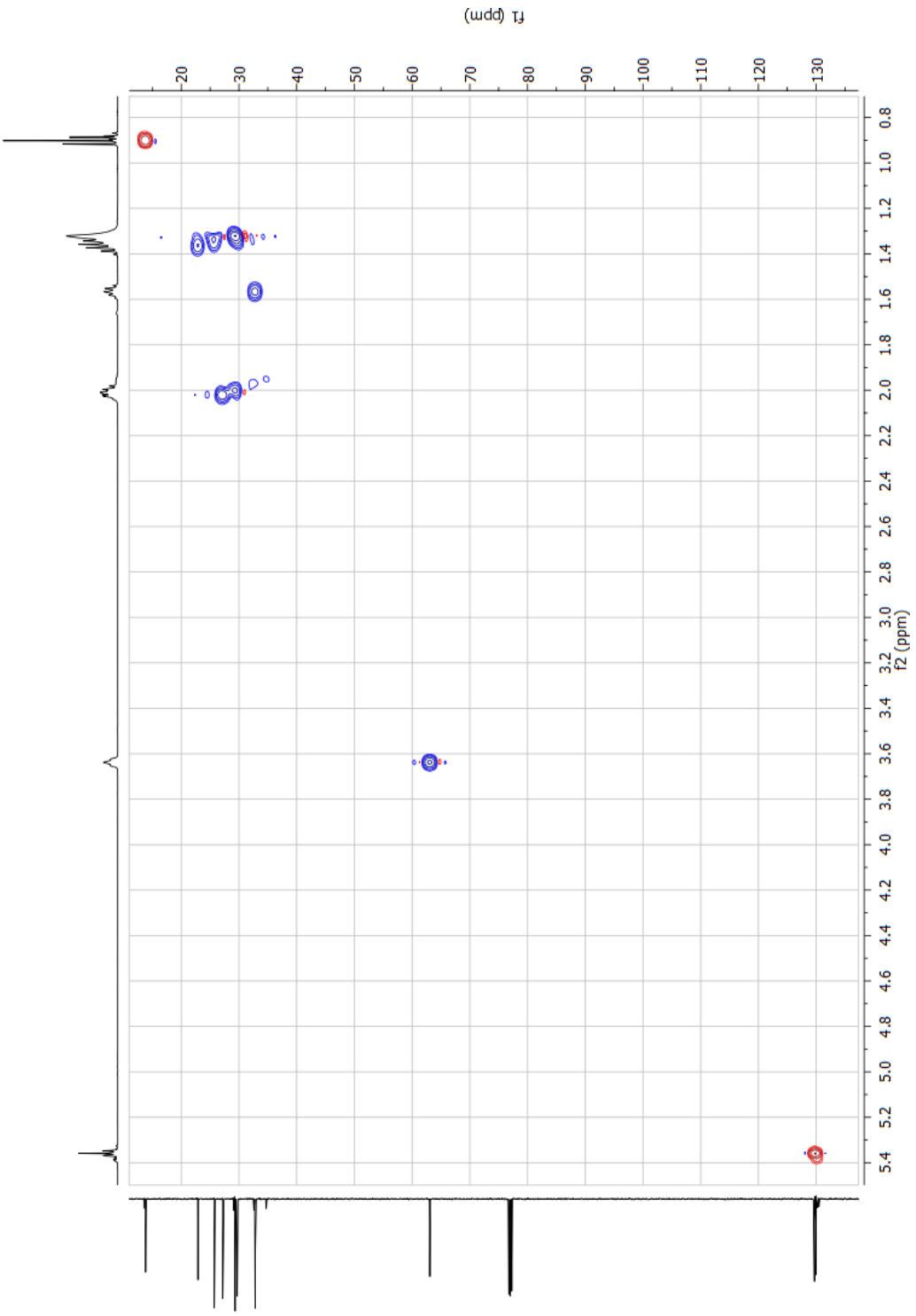


Figure 26: HSQC spectrum of (*Z*)-dodec-8-en-1-ol (**2.12**).

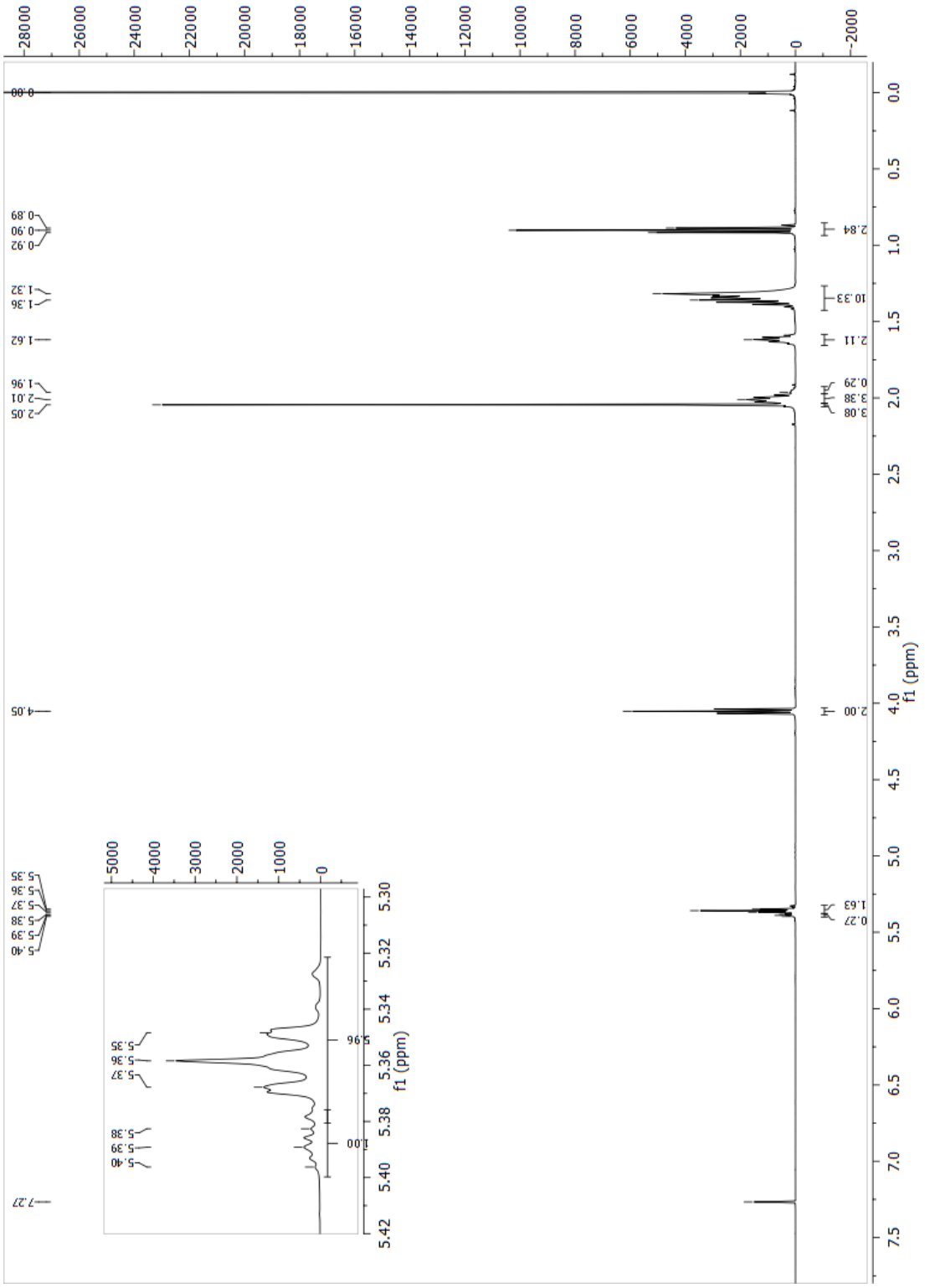


Figure 27: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (*Z*)-dodec-8-en-1-yl acetate (**2.13**).

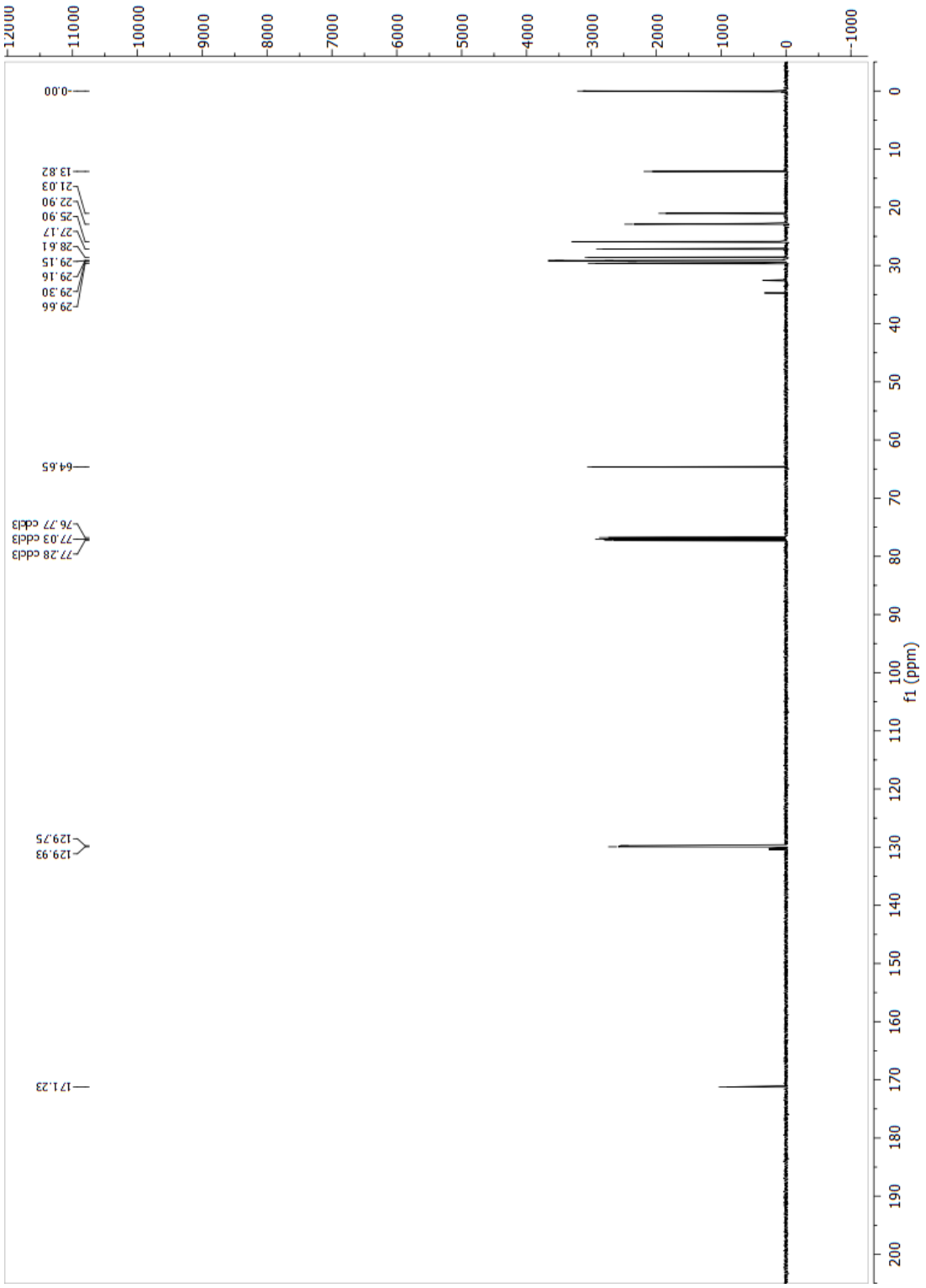


Figure 28: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (*Z*)-dodec-8-en-1-yl acetate (**2.13**).

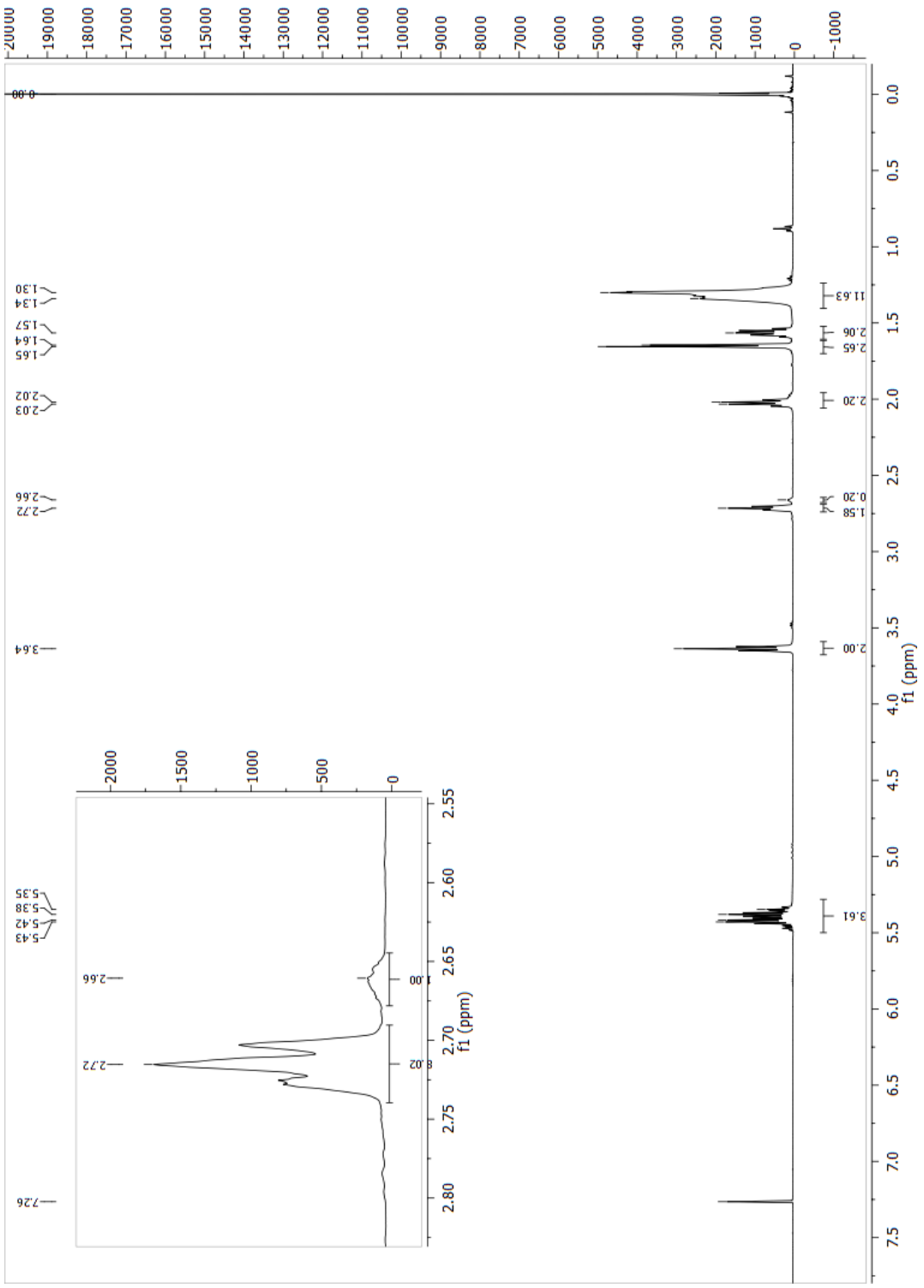


Figure 29: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (9*Z*,12*E*)-tetradeca-9,12-dien-1-ol (**2.15**).

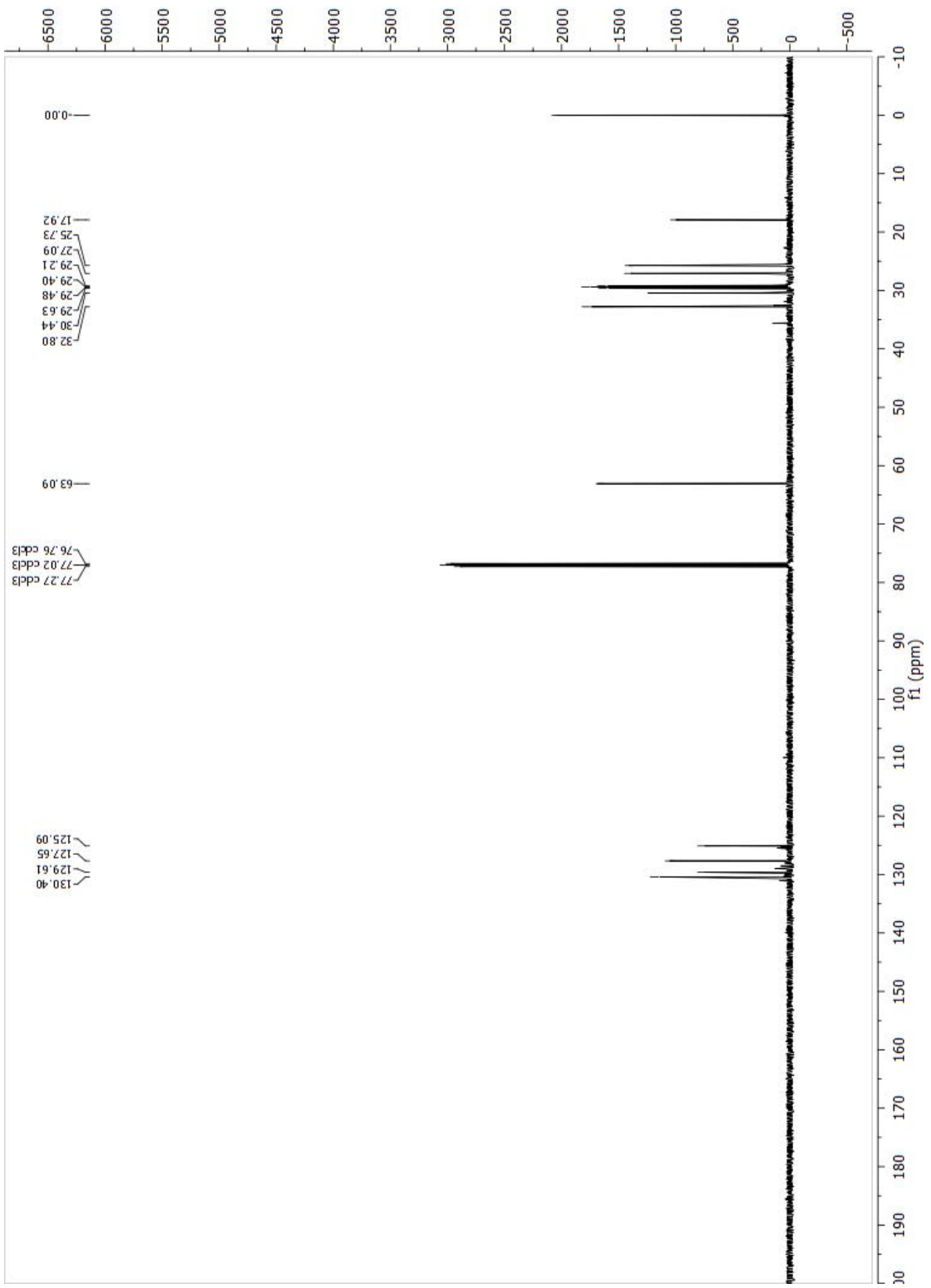


Figure 30: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (9*Z*,12*E*)-tetradeca-9,12-dien-1-ol (**2.15**).

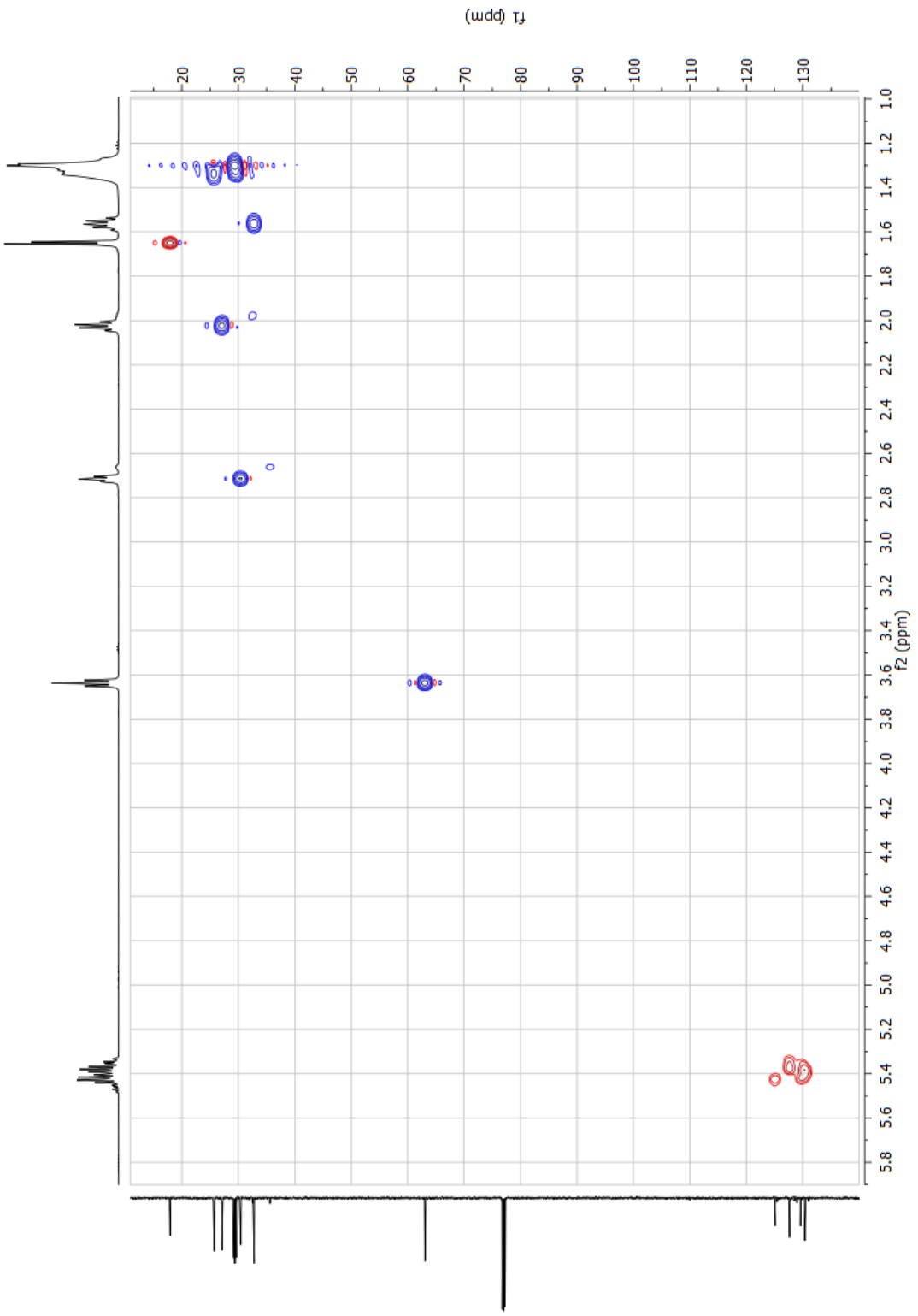


Figure 31: HSQC spectrum of (9*Z*,12*E*)-tetradeca-9,12-dien-1-ol (**2.15**).

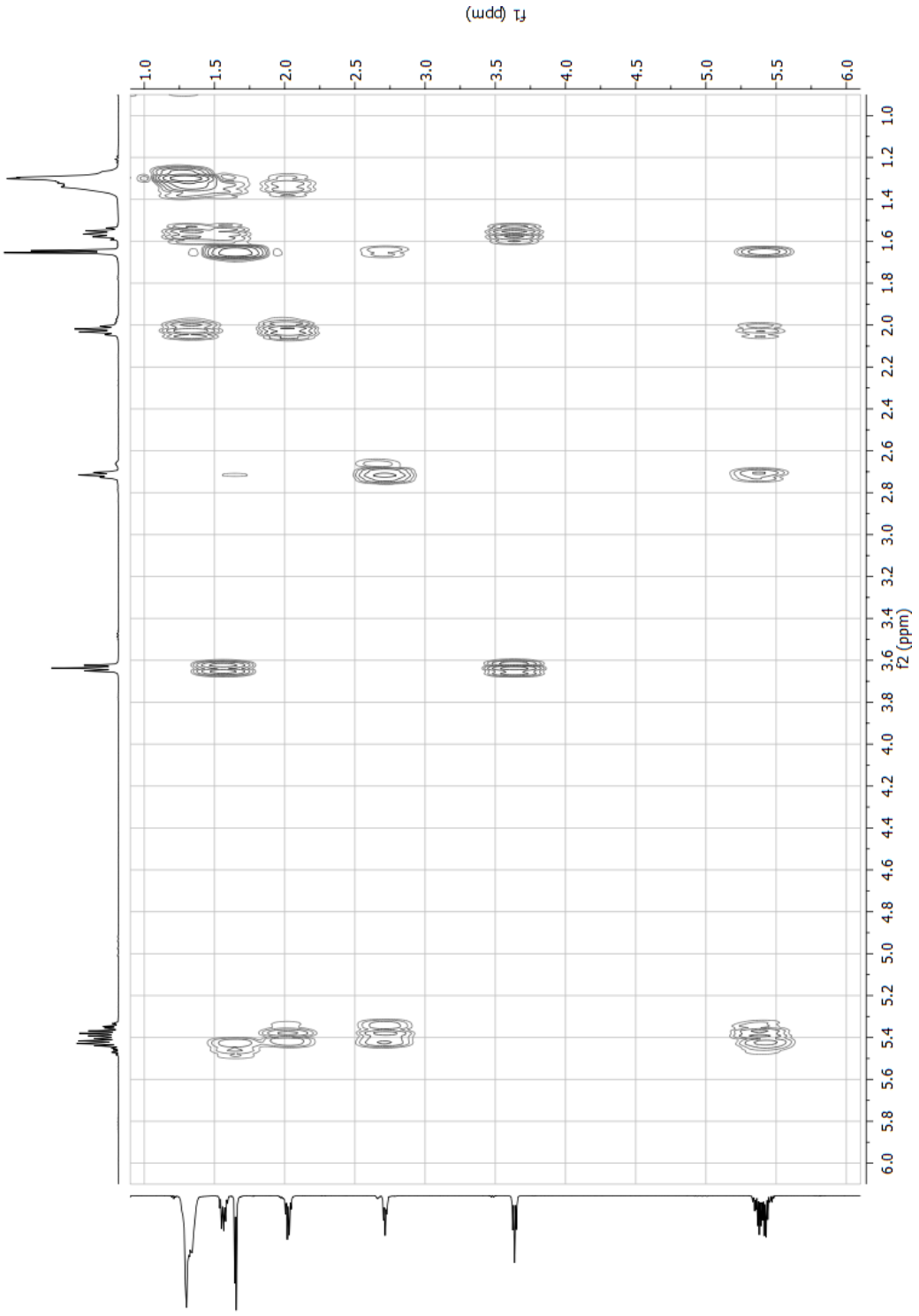


Figure 32: COSY spectrum of (9*Z*,12*E*)-tetradeca-9,12-dien-1-ol (**2.15**).

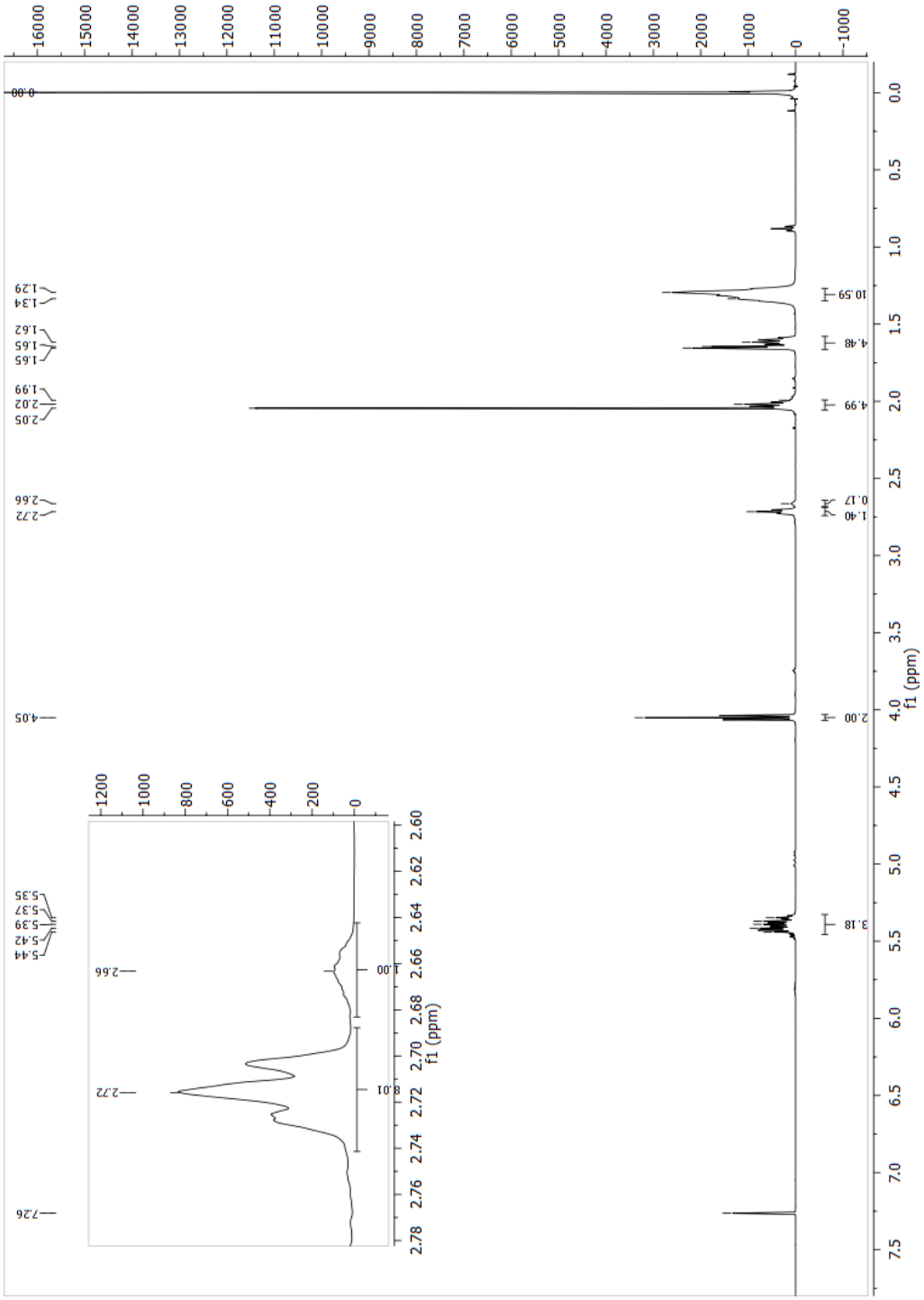


Figure 33: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (9*Z*,12*E*)-tetradeca-9,12-dien-1-yl acetate (**2.16**).

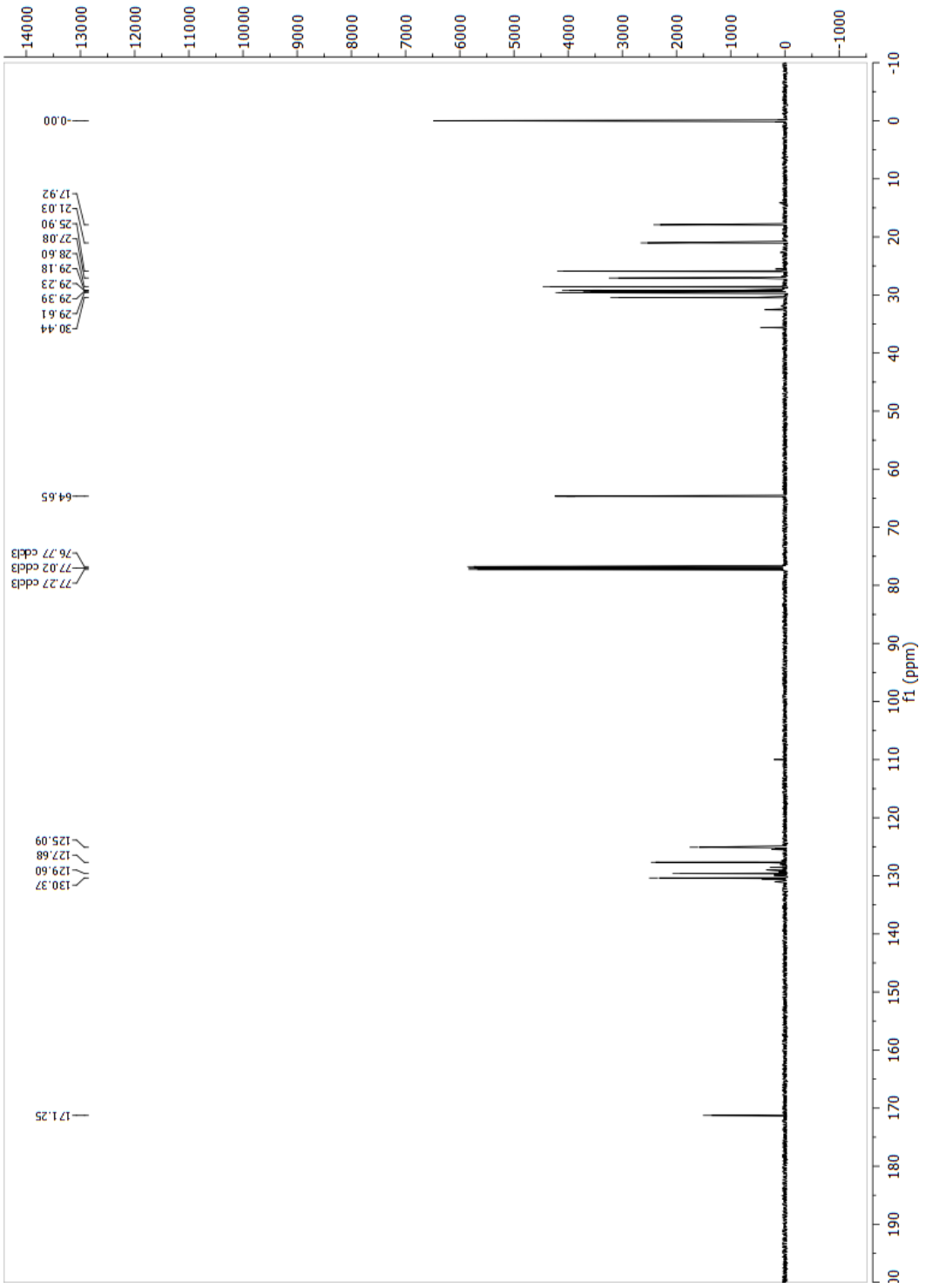


Figure 34: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (9*Z*,12*E*)-tetradeca-9,12-dien-1-yl acetate (**2.16**).

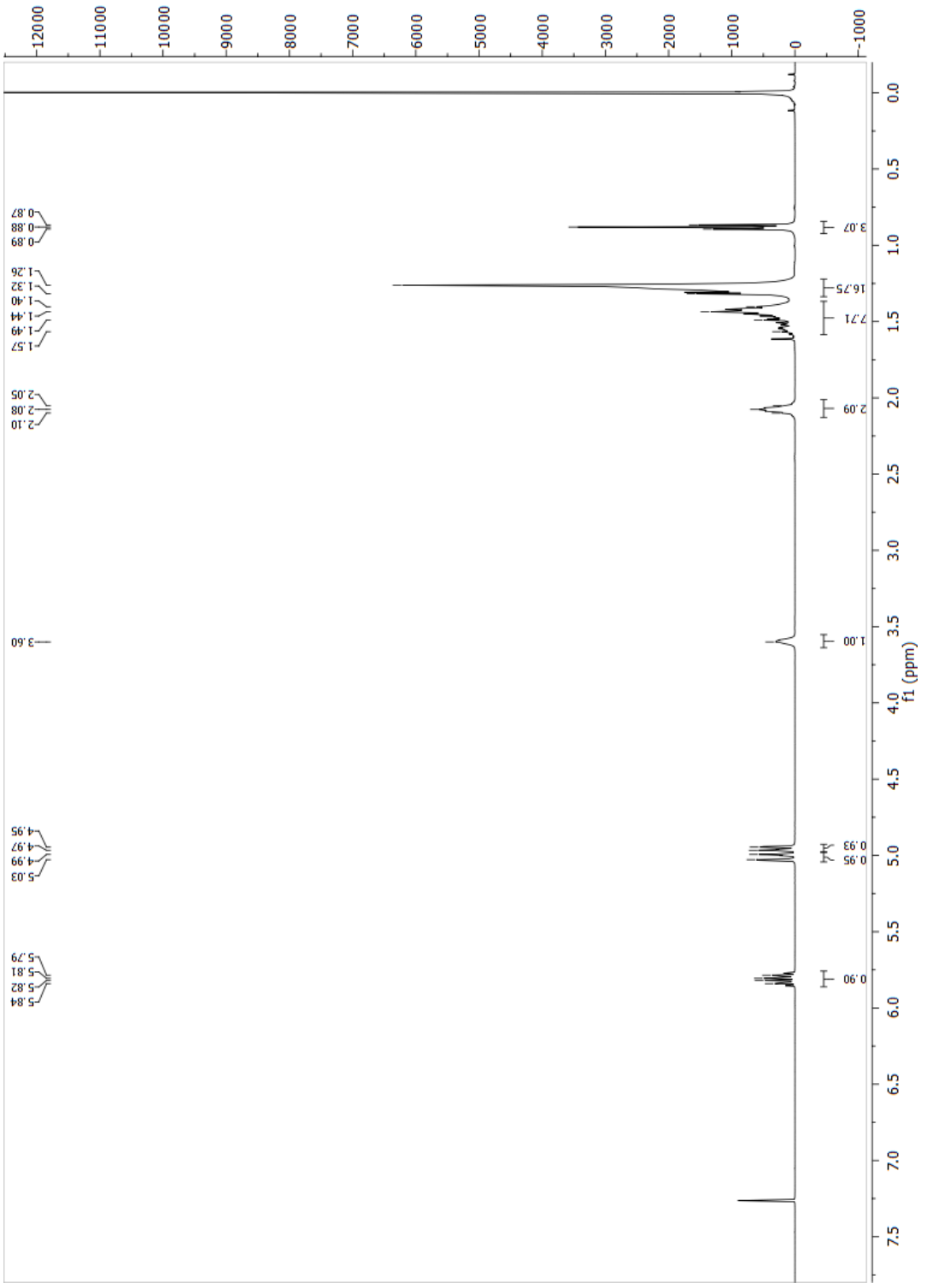


Figure 35: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of hexadec-1-en-6-ol (**2.18**).

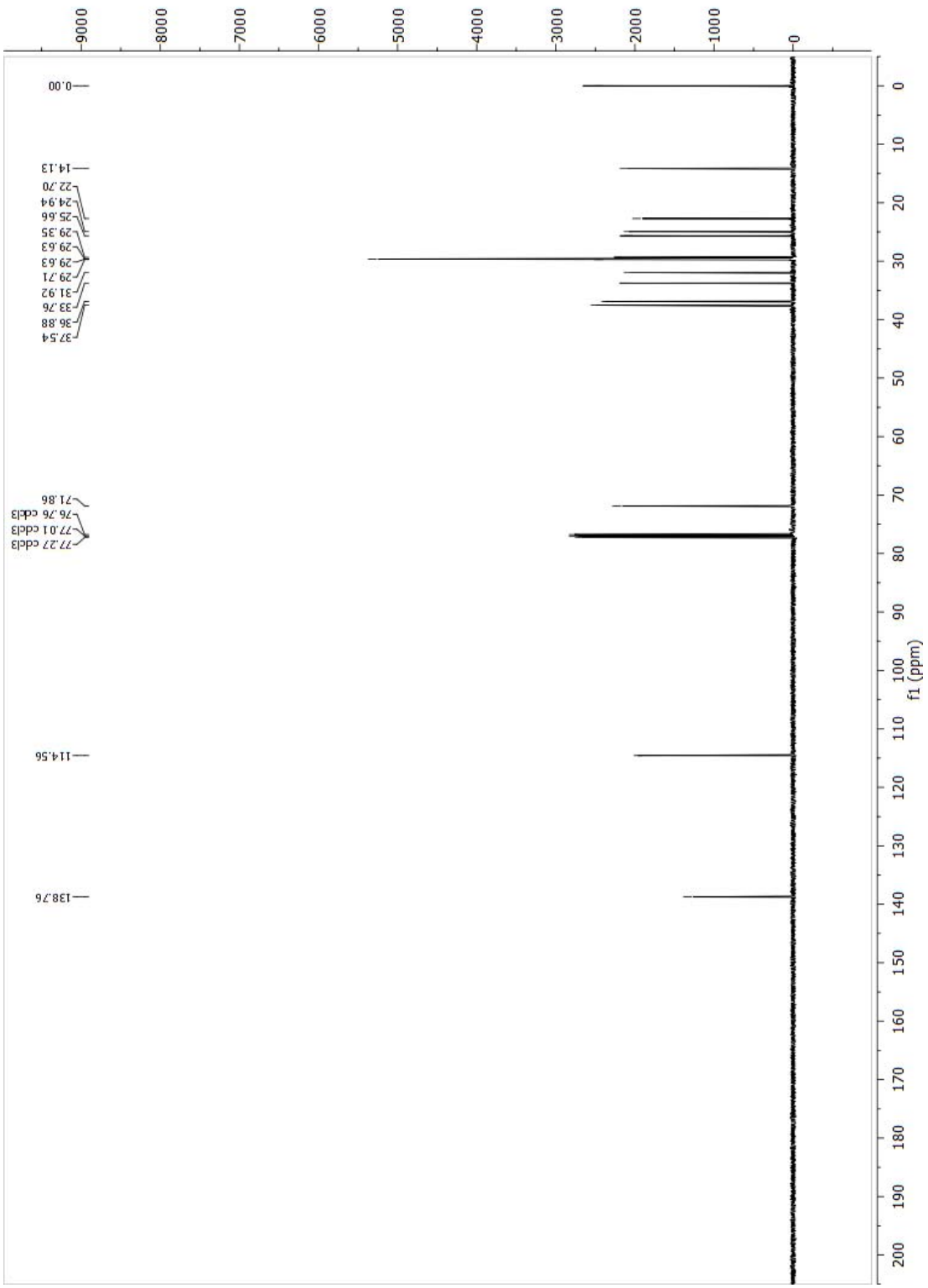


Figure 36: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of hexadec-1-en-6-ol (**2.18**).

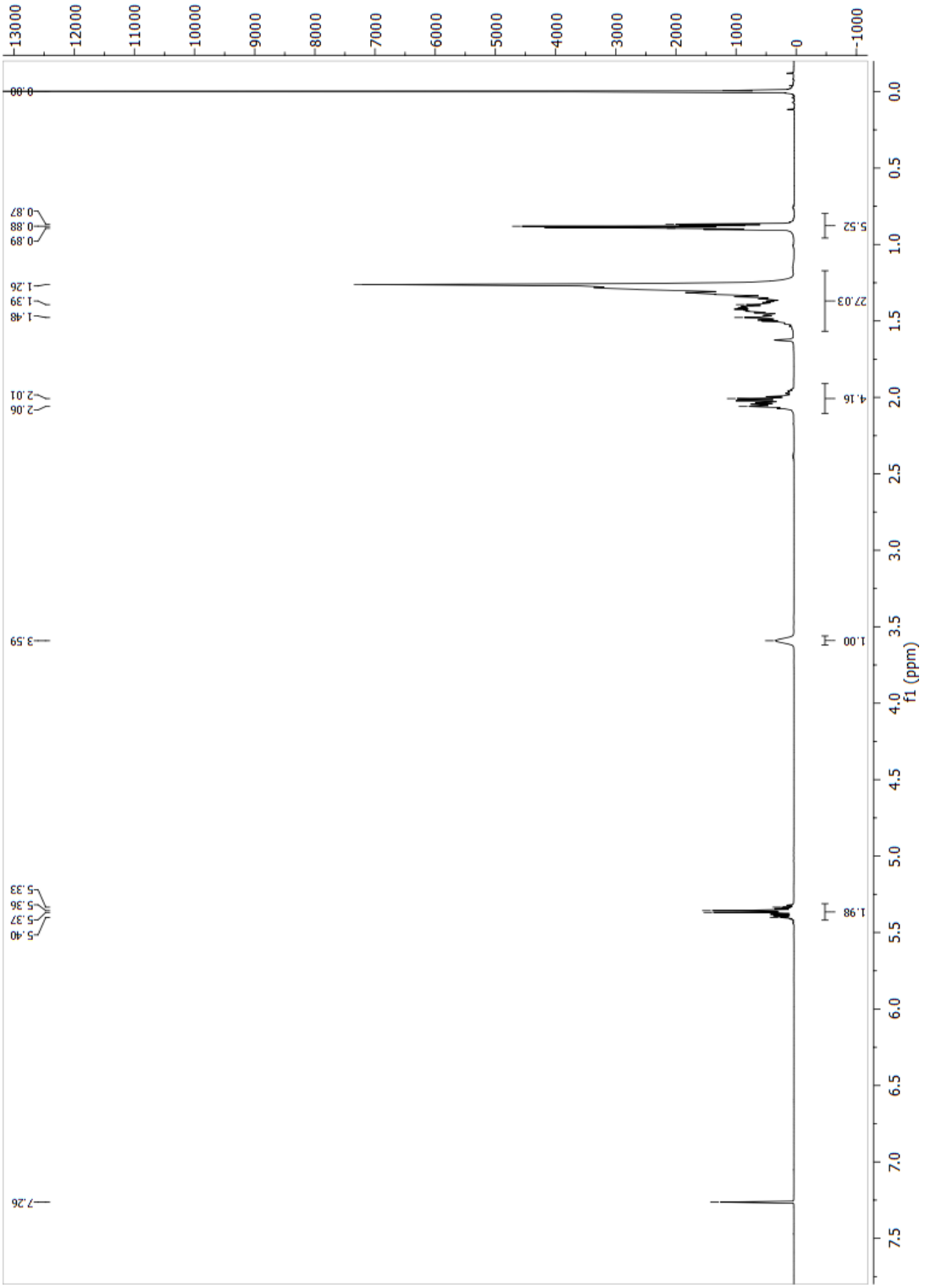


Figure 37: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (*Z*)-henicos-6-en-11-ol (**2.19**).

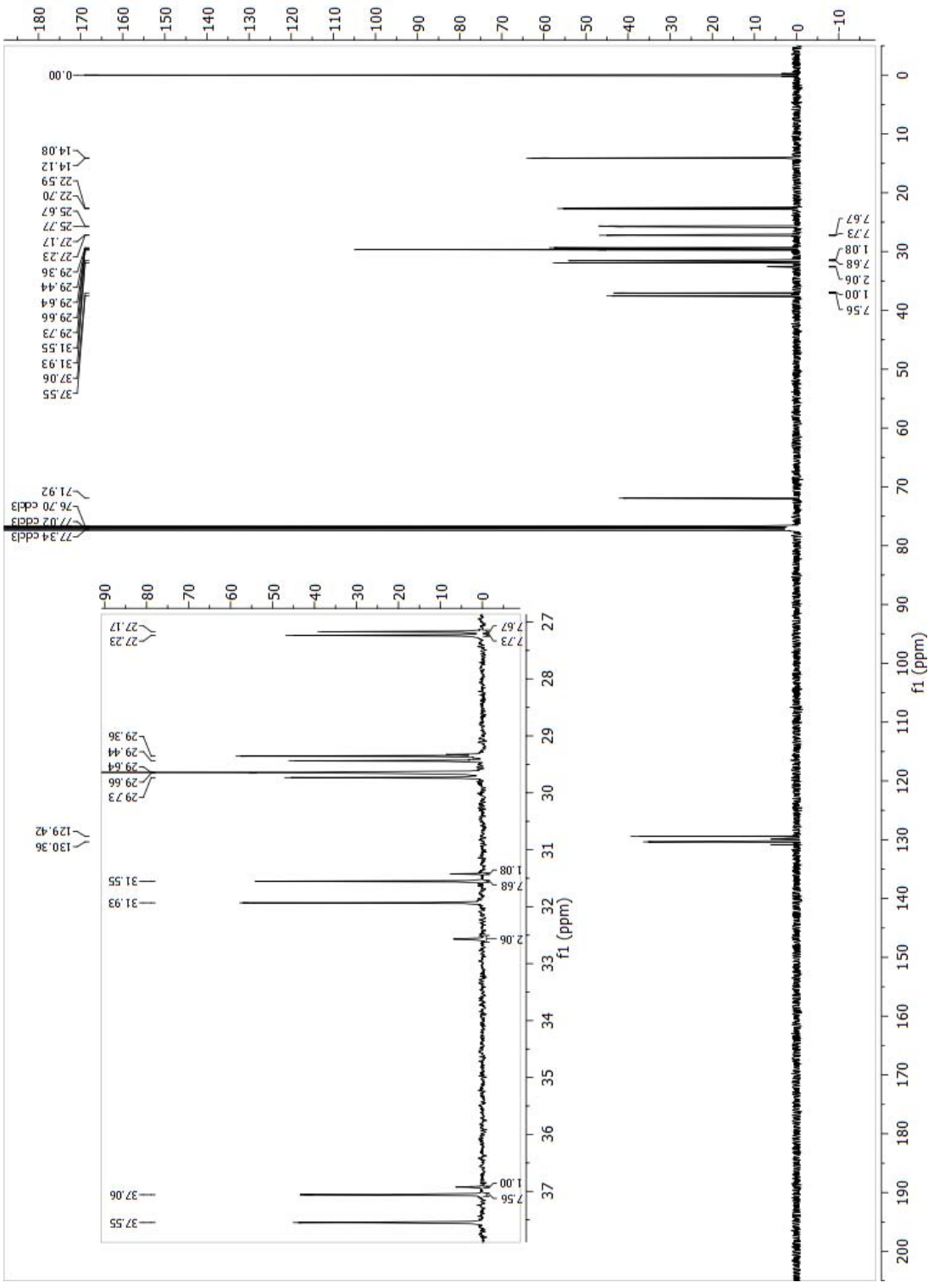


Figure 38: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (*Z*)-henicos-6-en-11-ol (**2.19**).

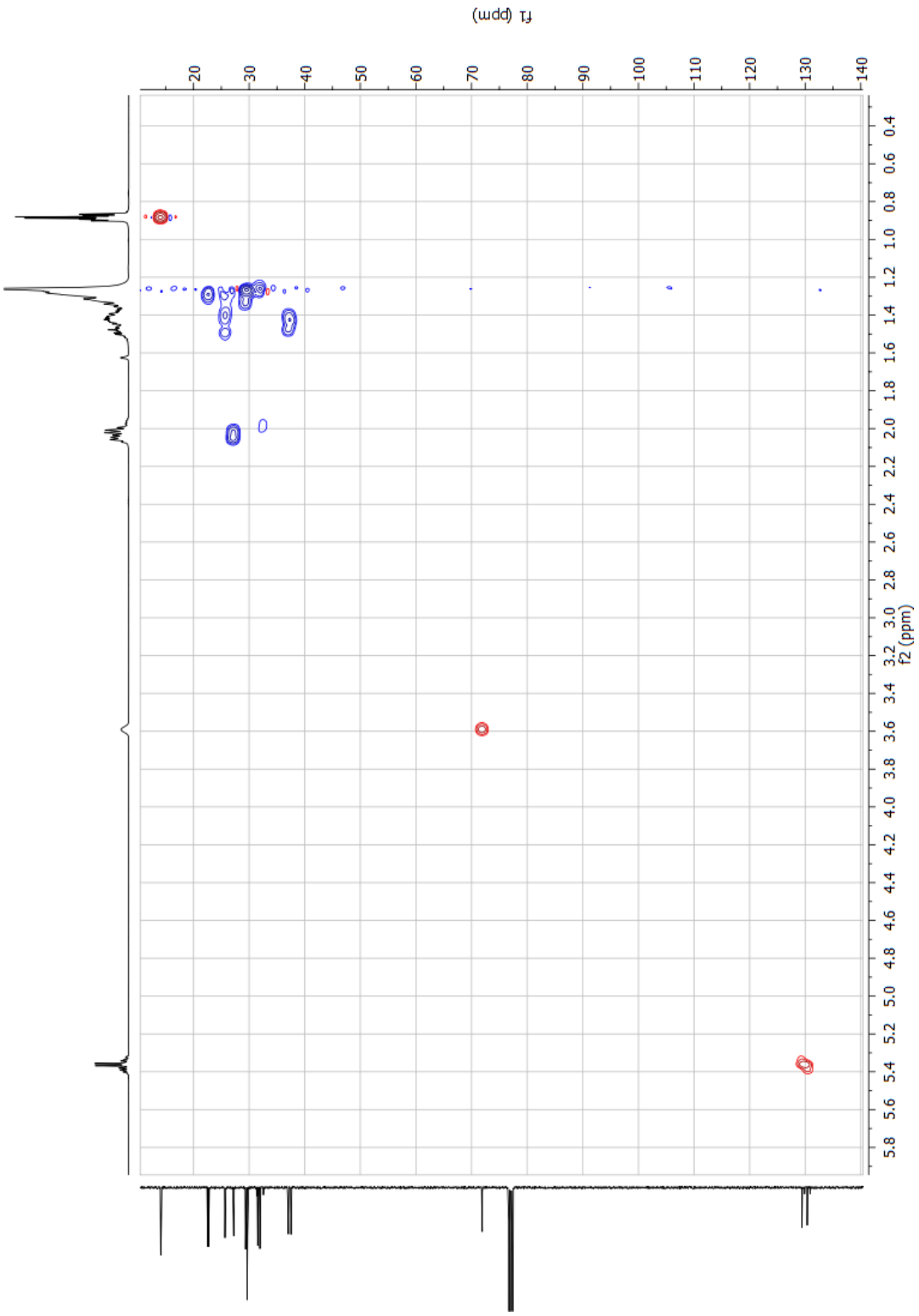


Figure 39: HSQC spectrum of (*Z*)-henicos-6-en-11-ol (**2.19**).

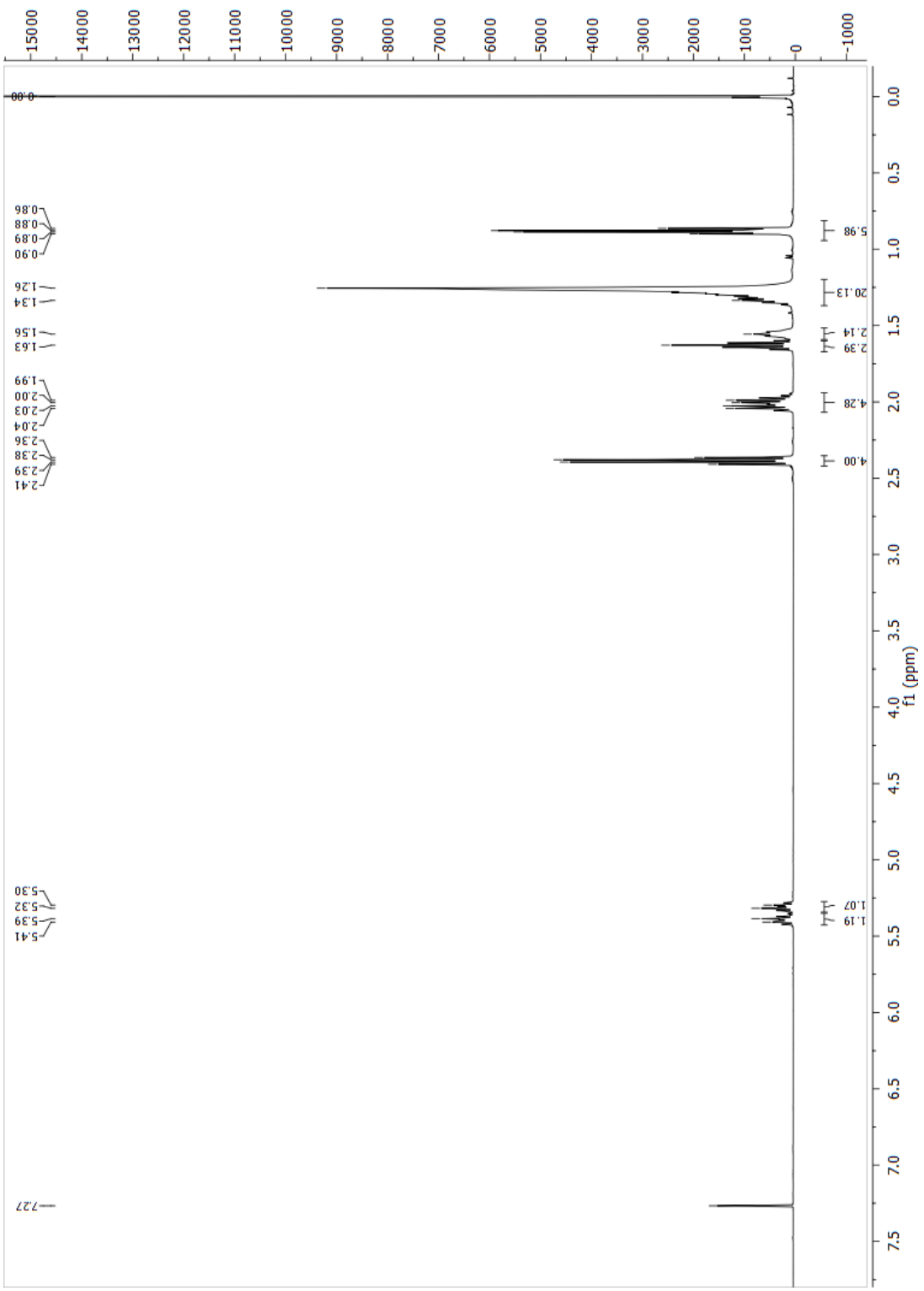


Figure 40: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (*Z*)-henicos-6-en-11-one (**2.20**).

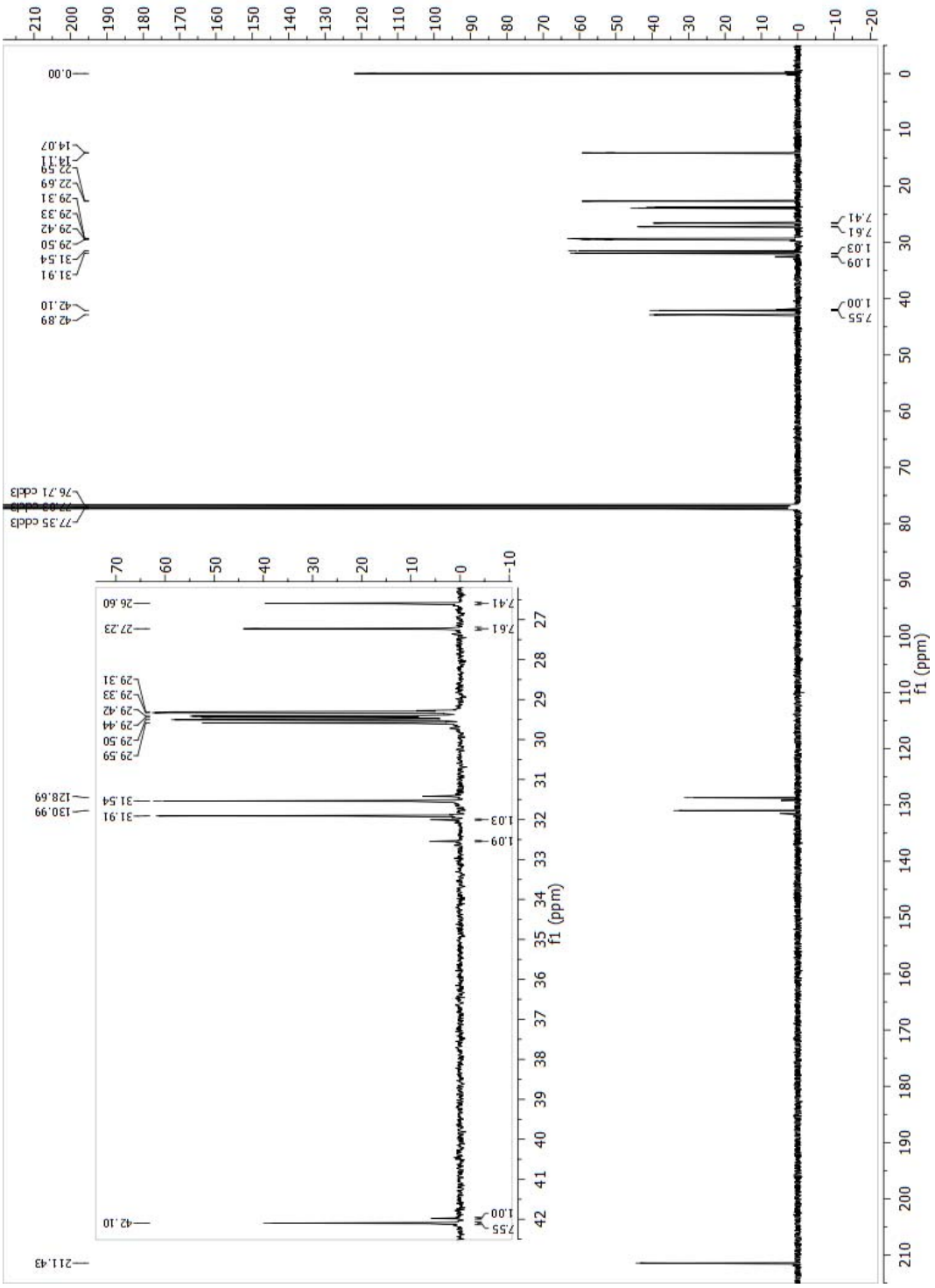


Figure 41: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (*Z*)-henicos-6-en-11-one (**2.20**).

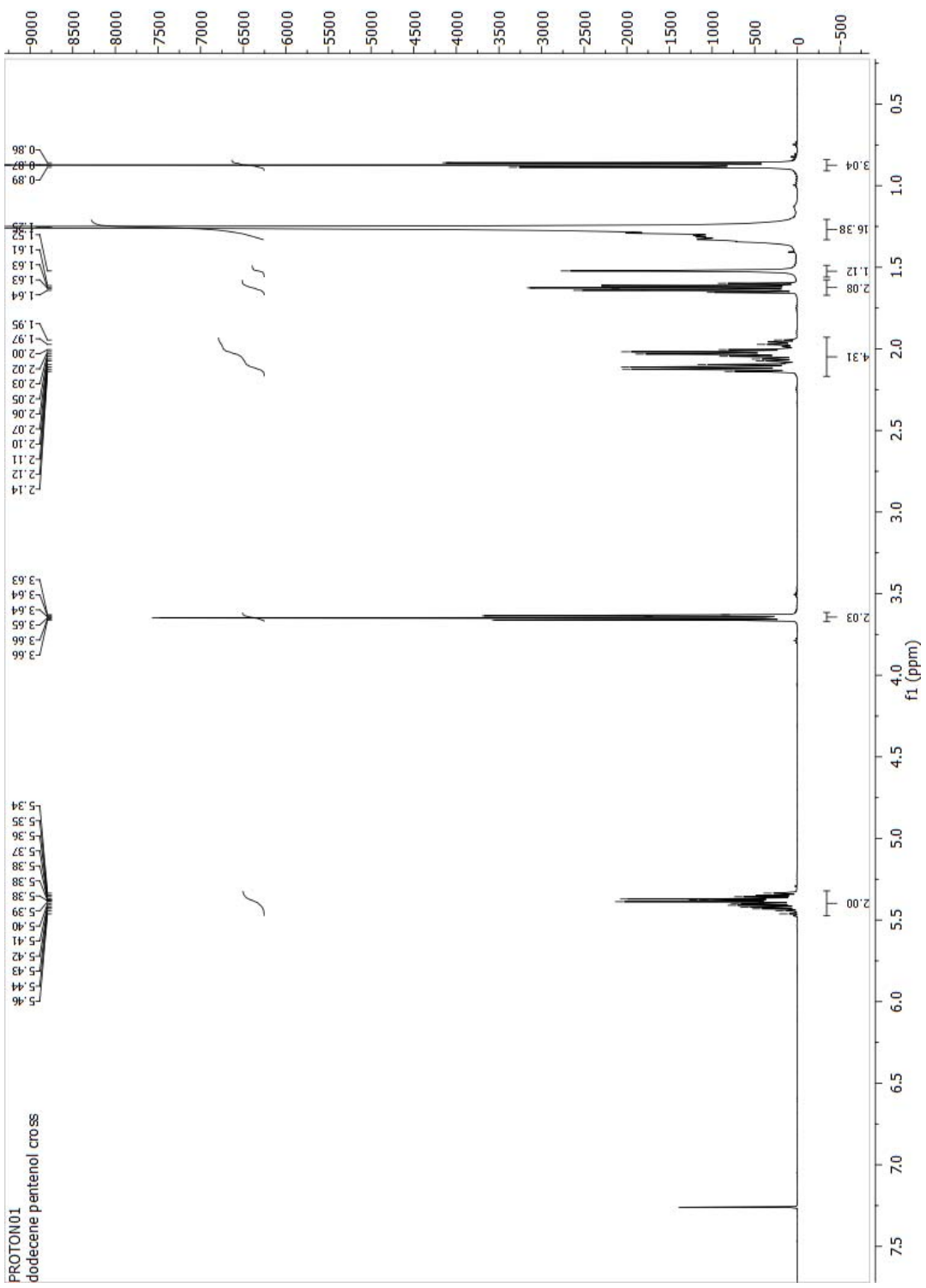


Figure 42: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (*Z*)-Pentadec-4-en-1-ol (**2.21**).

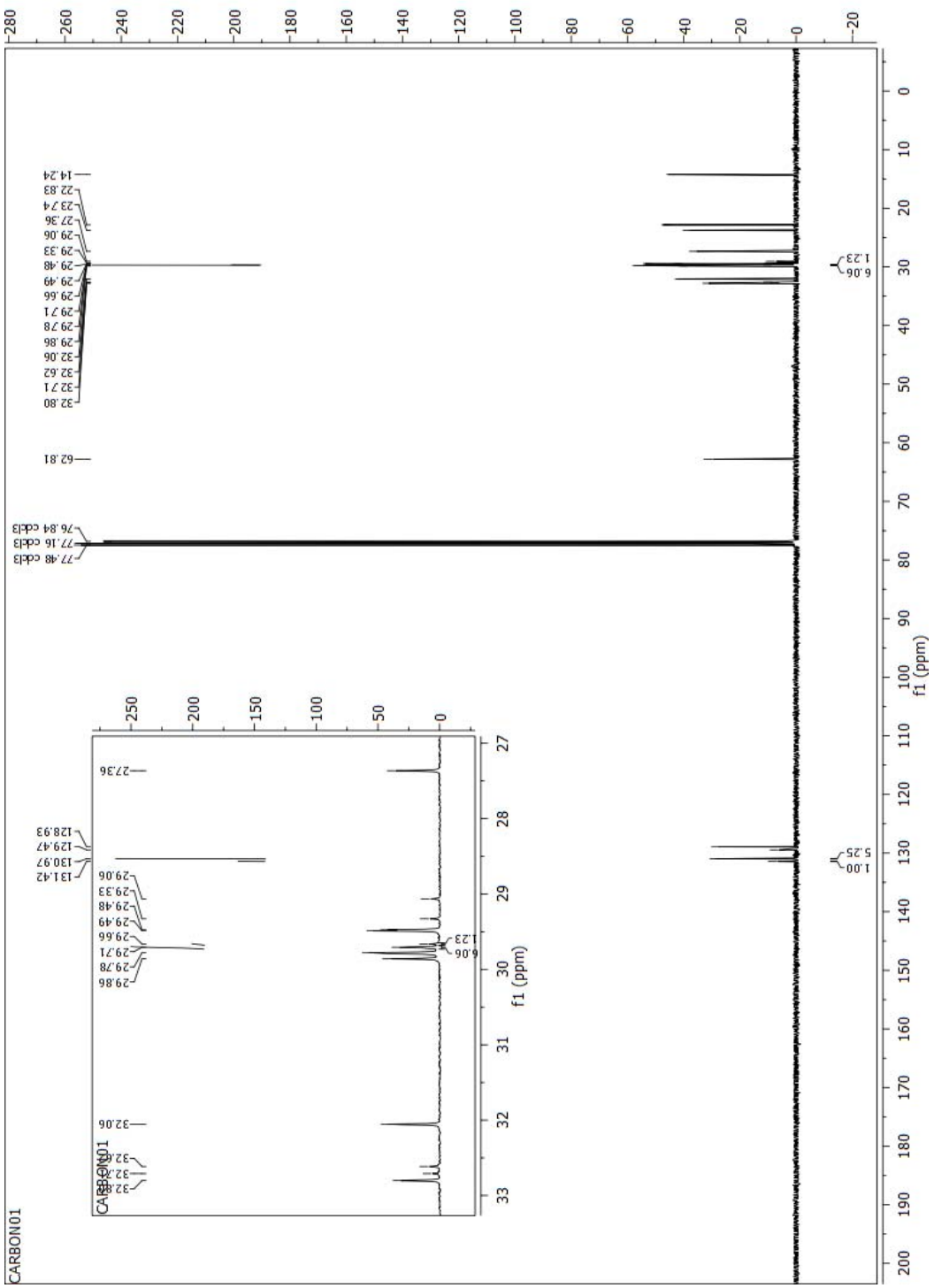


Figure 43: ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of (*Z*)-Pentadec-4-en-1-ol (**2.21**).

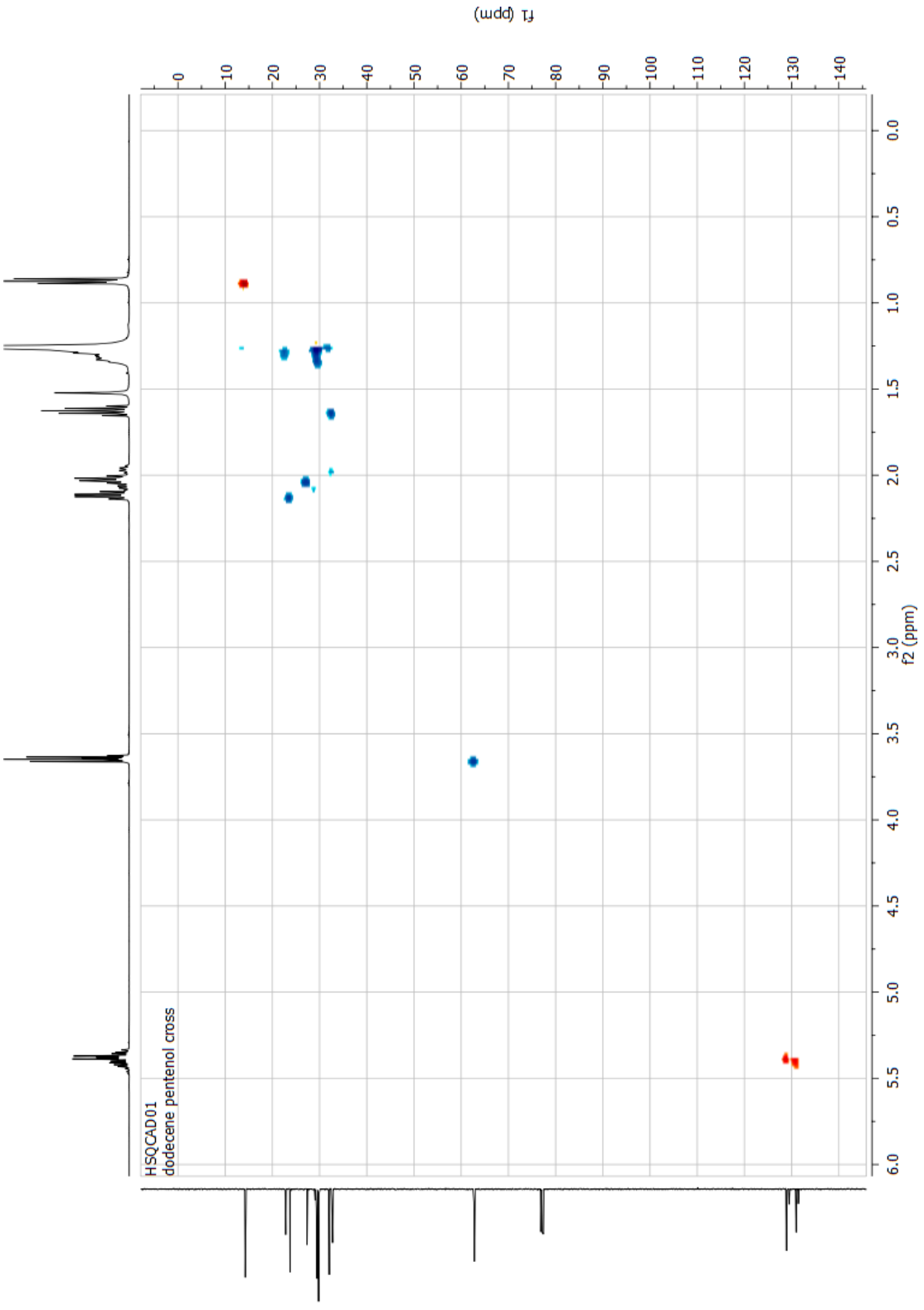


Figure 44: HSQC spectrum of (*Z*)-Pentadec-4-en-1-ol (**2.21**).

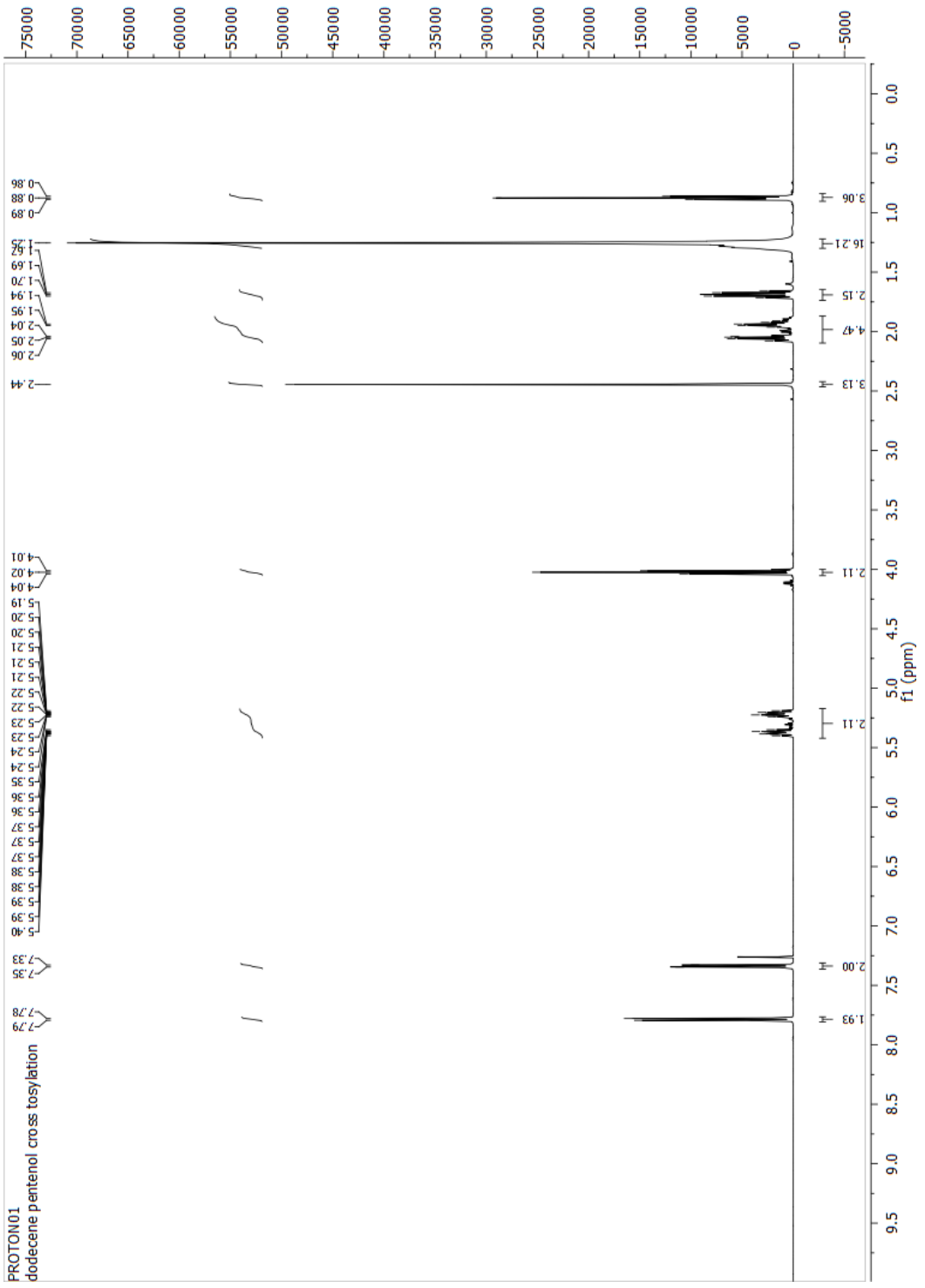


Figure 45: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (*Z*)-Pentadecen-4-en-1-yl 4-methylbenzenesulfonate (**2.22**).

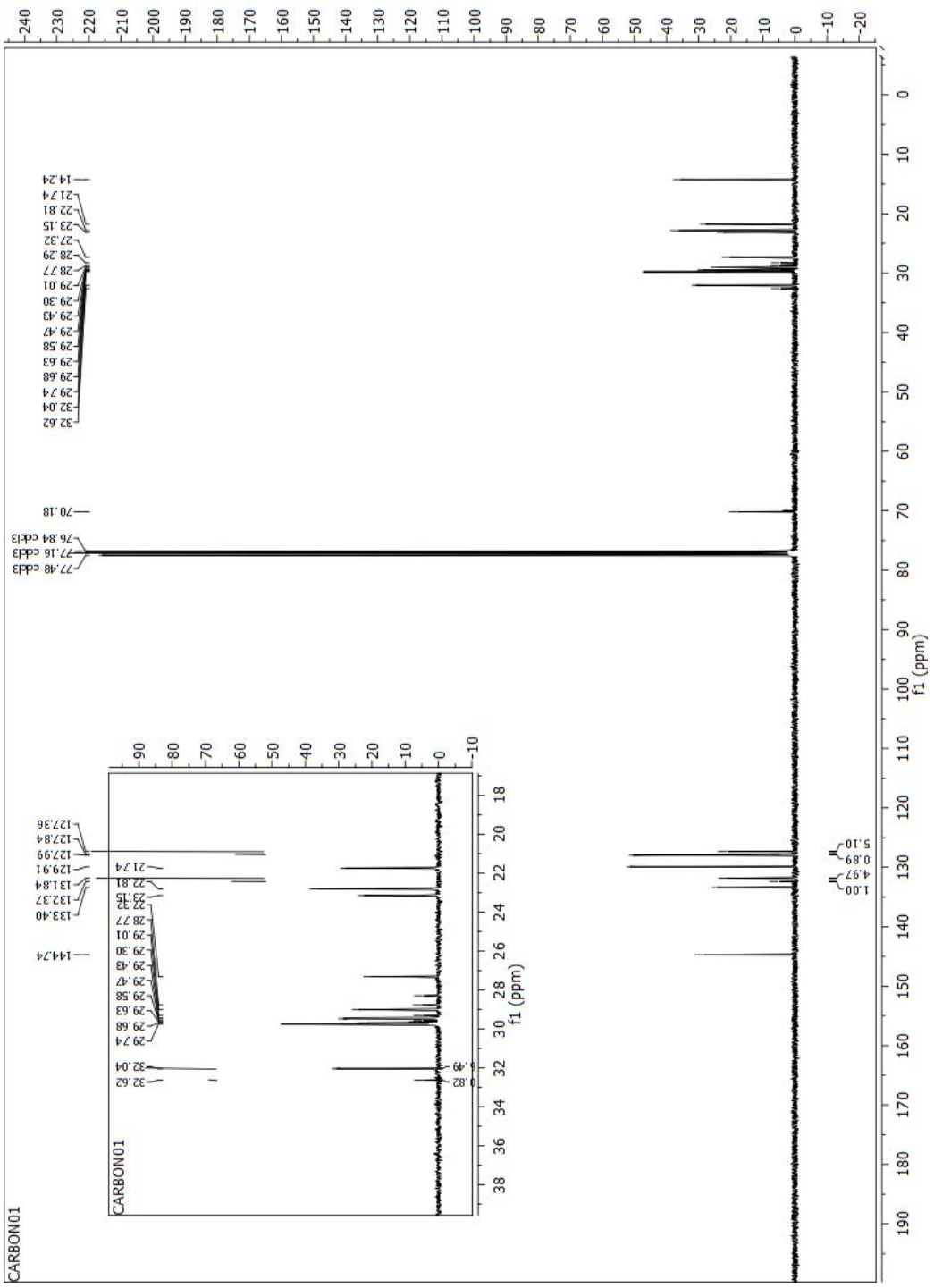


Figure 46: ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of (*Z*)-Pentadecen-4-en-1-yl 4-methylbenzenesulfonate (**2.22**).

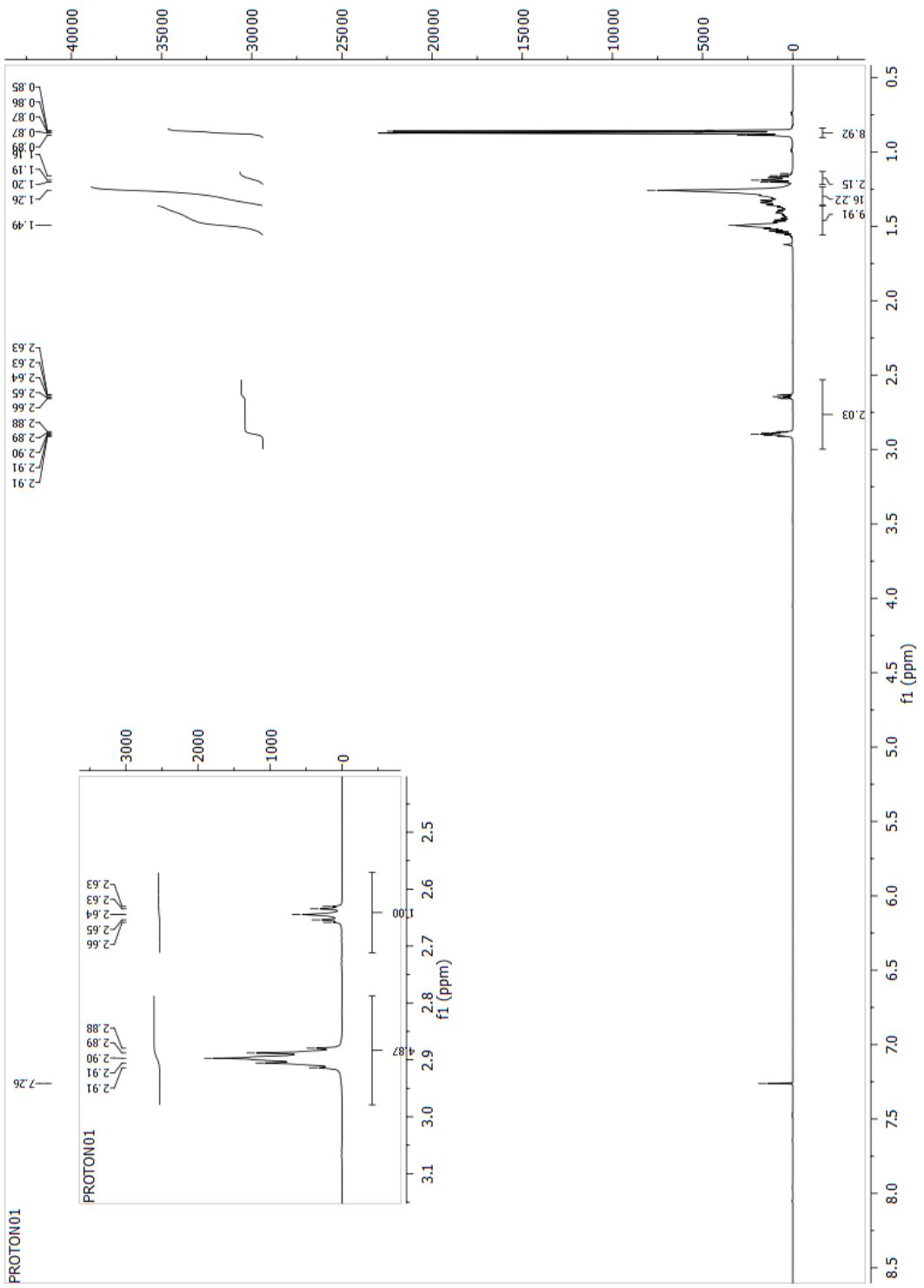
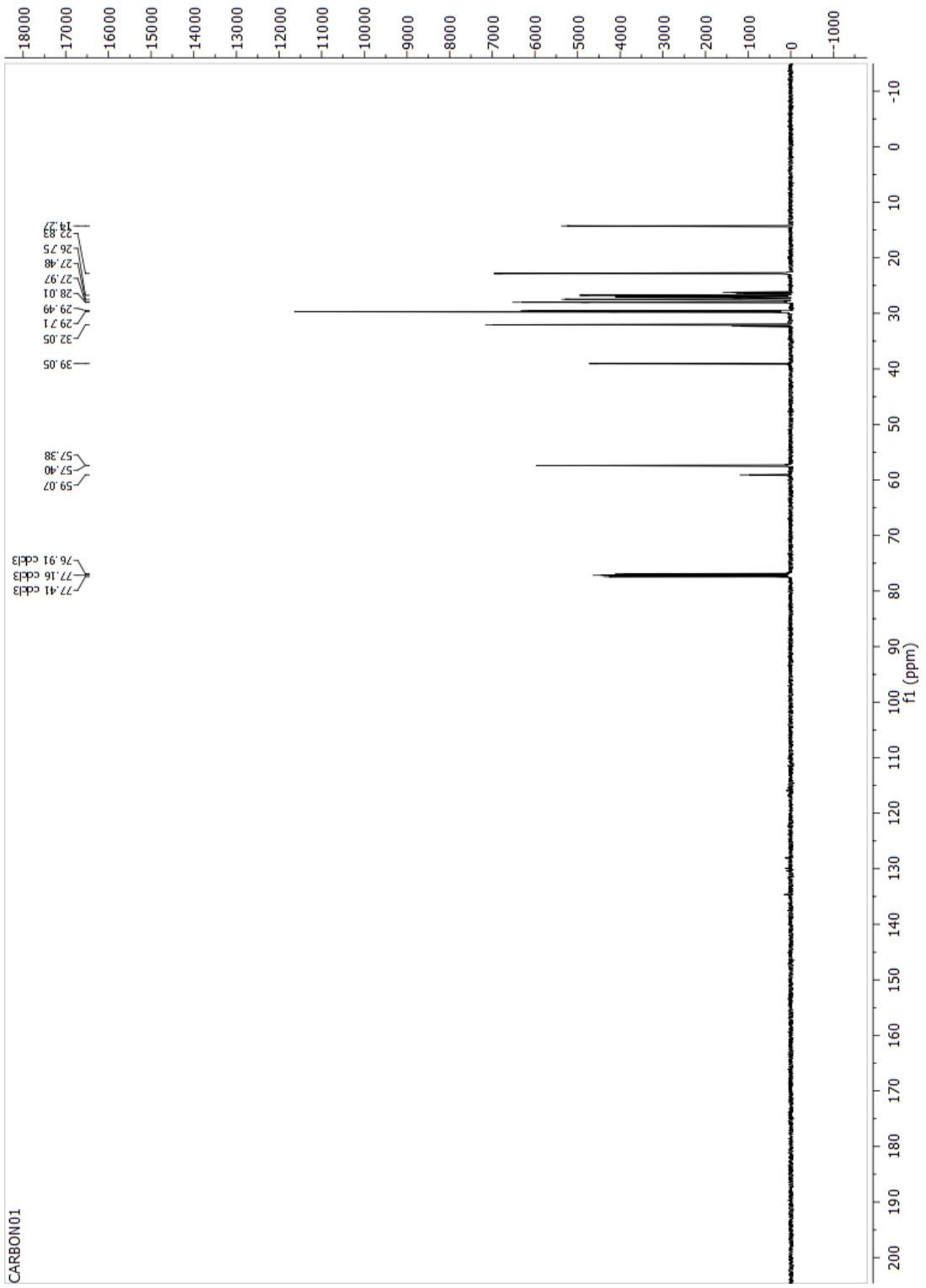


Figure 47: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *cis*-7,8-Epoxy-2-methyloctadecane (±)-**2.24**.



Fgure 48: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *cis*-7,8-Epoxy-2-methyloctadecane (±)-**2.24**.

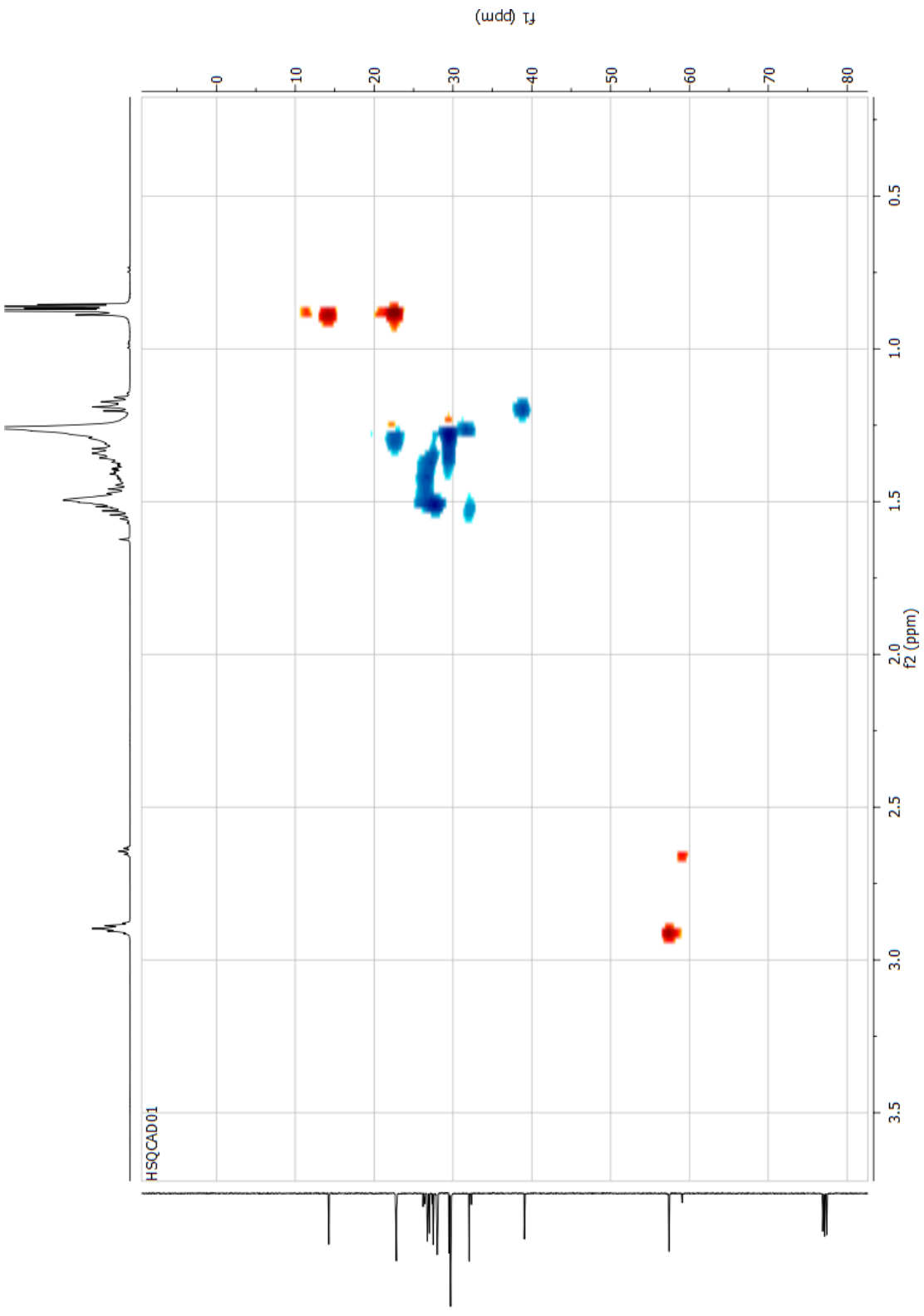


Figure 49: HSQC spectrum of *cis*-7,8-Epoxy-2-methyloctadecane (±)-**2.24**.

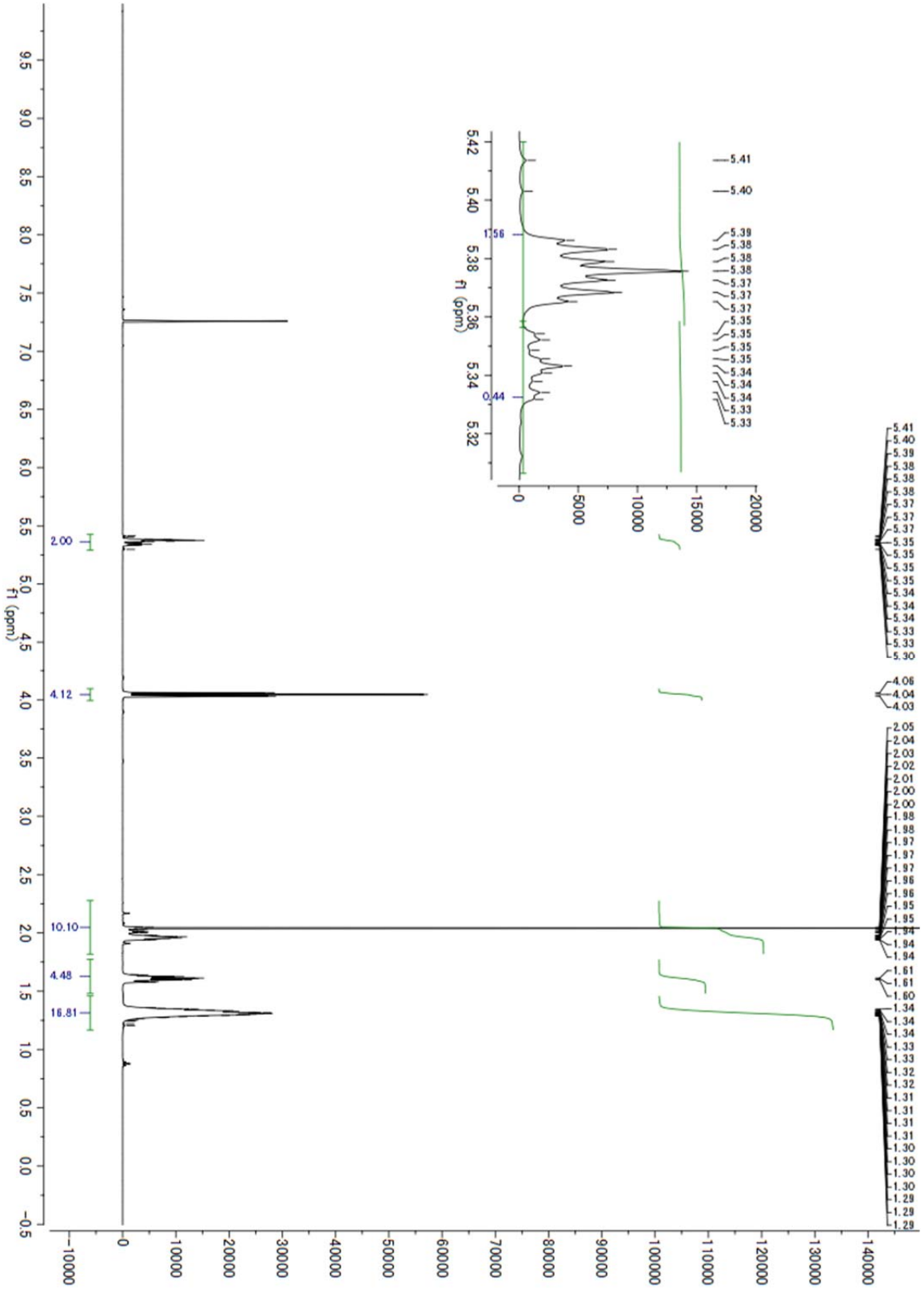


Figure 50: ^{1}H NMR (500 MHz) spectrum of **2.34** in $CDCl_3$.

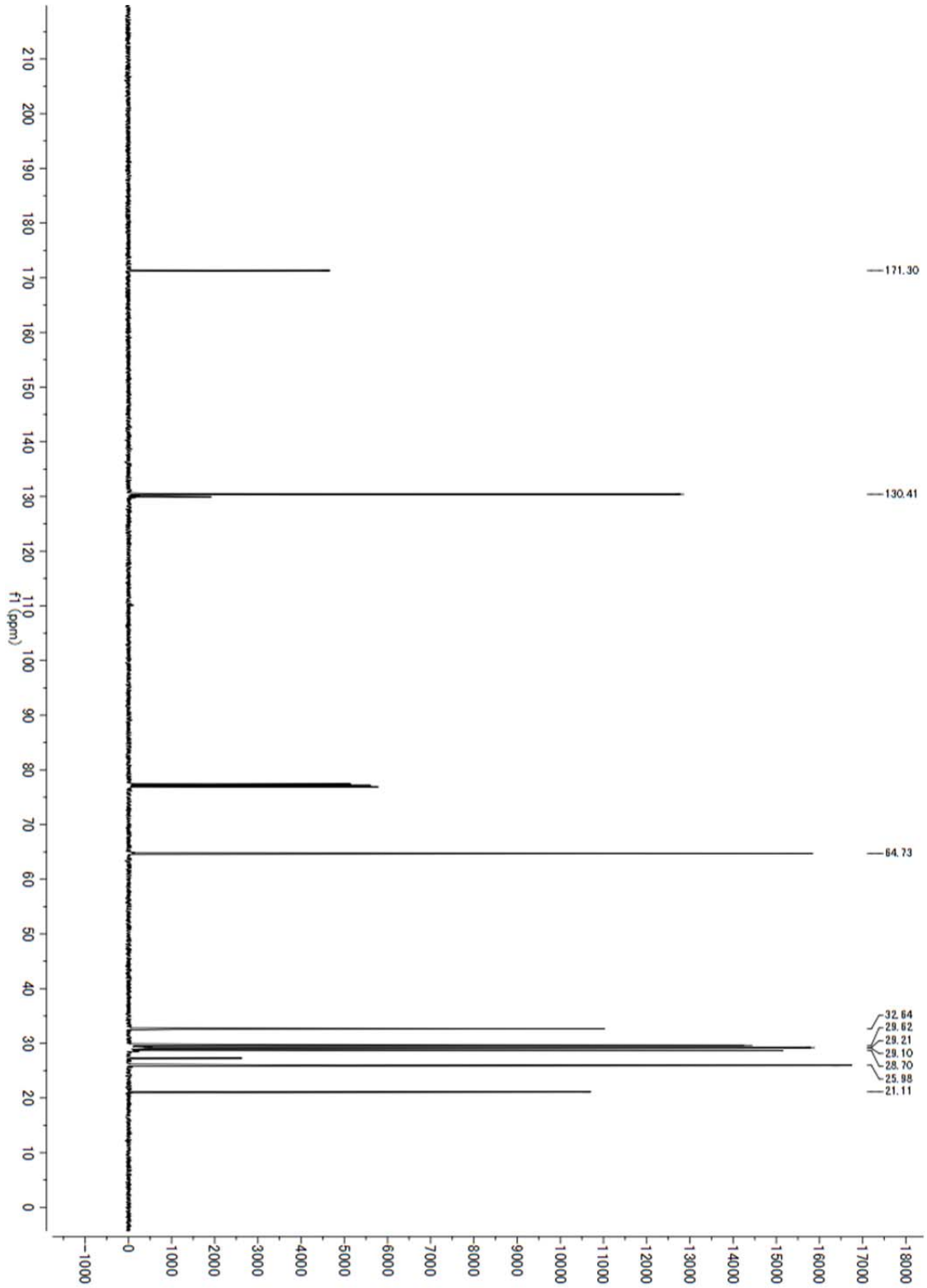


Figure 51: ^{13}C NMR (126 MHz) spectrum of **2.34** in $CDCl_3$.

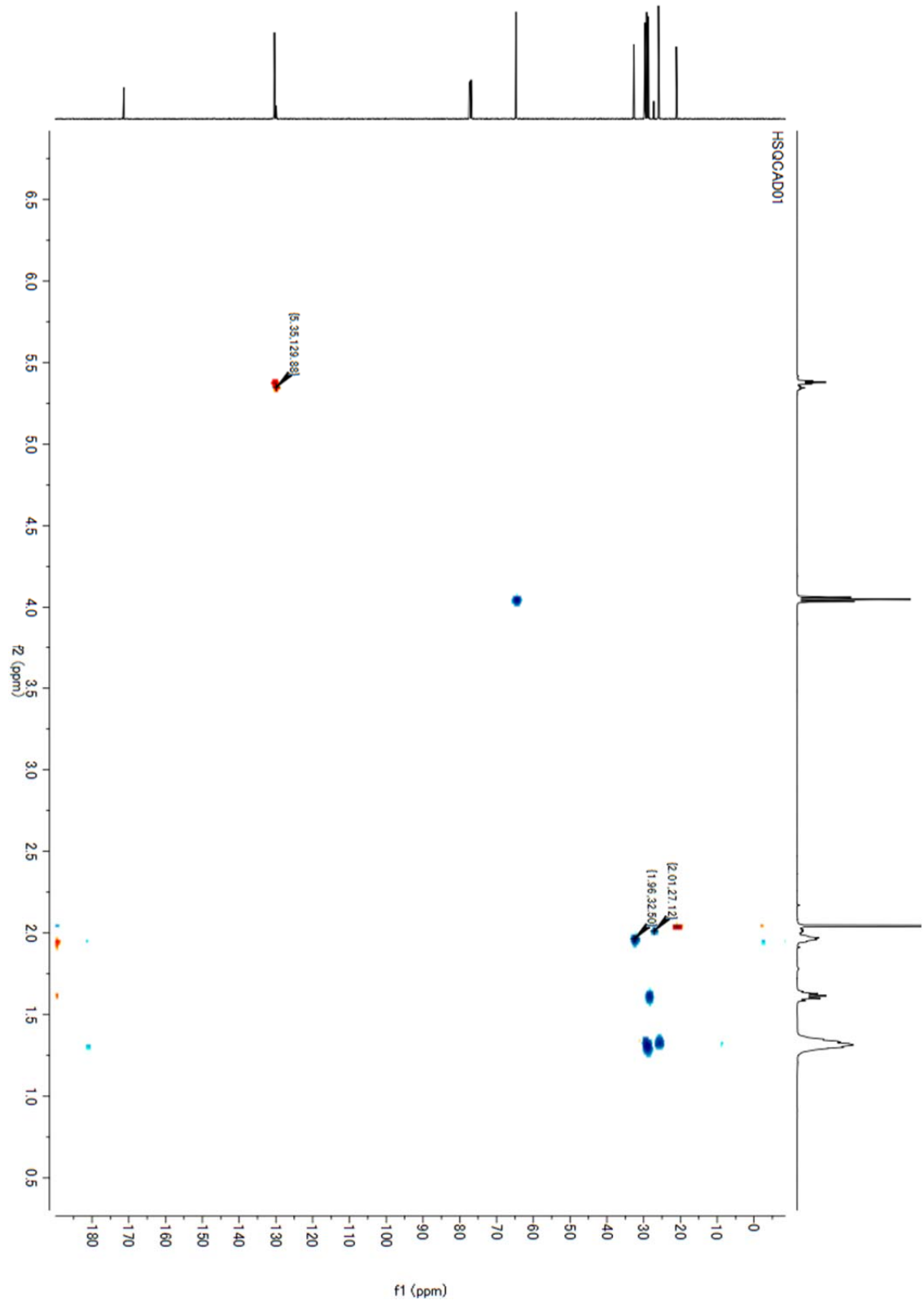


Figure 52: ^{1}H-^{13}C HSQC of **2.34** in $CDCl_3$.

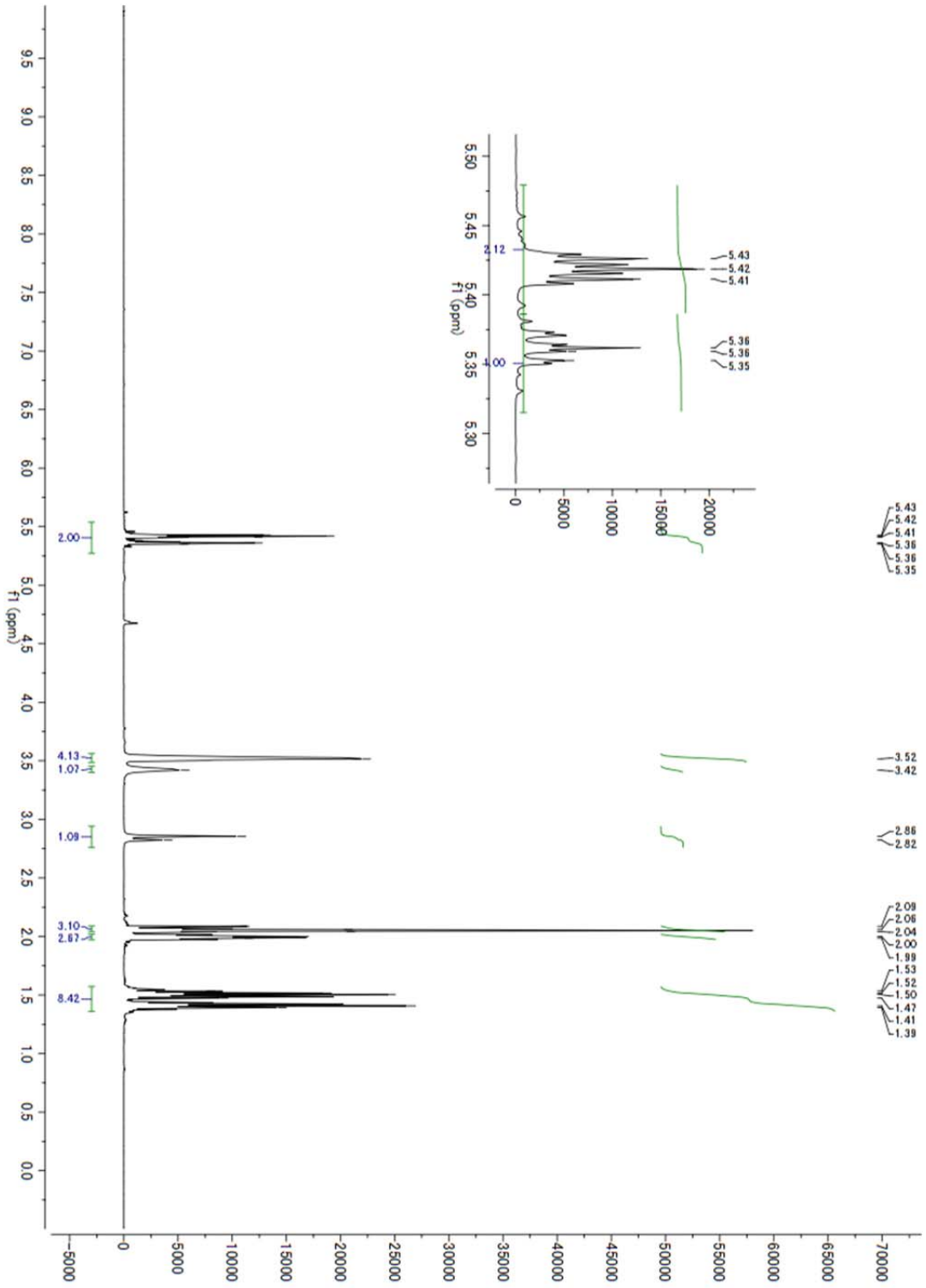


Figure 53: ^{1}H NMR (500 MHz) spectrum of **2.37** in acetone-d_6.

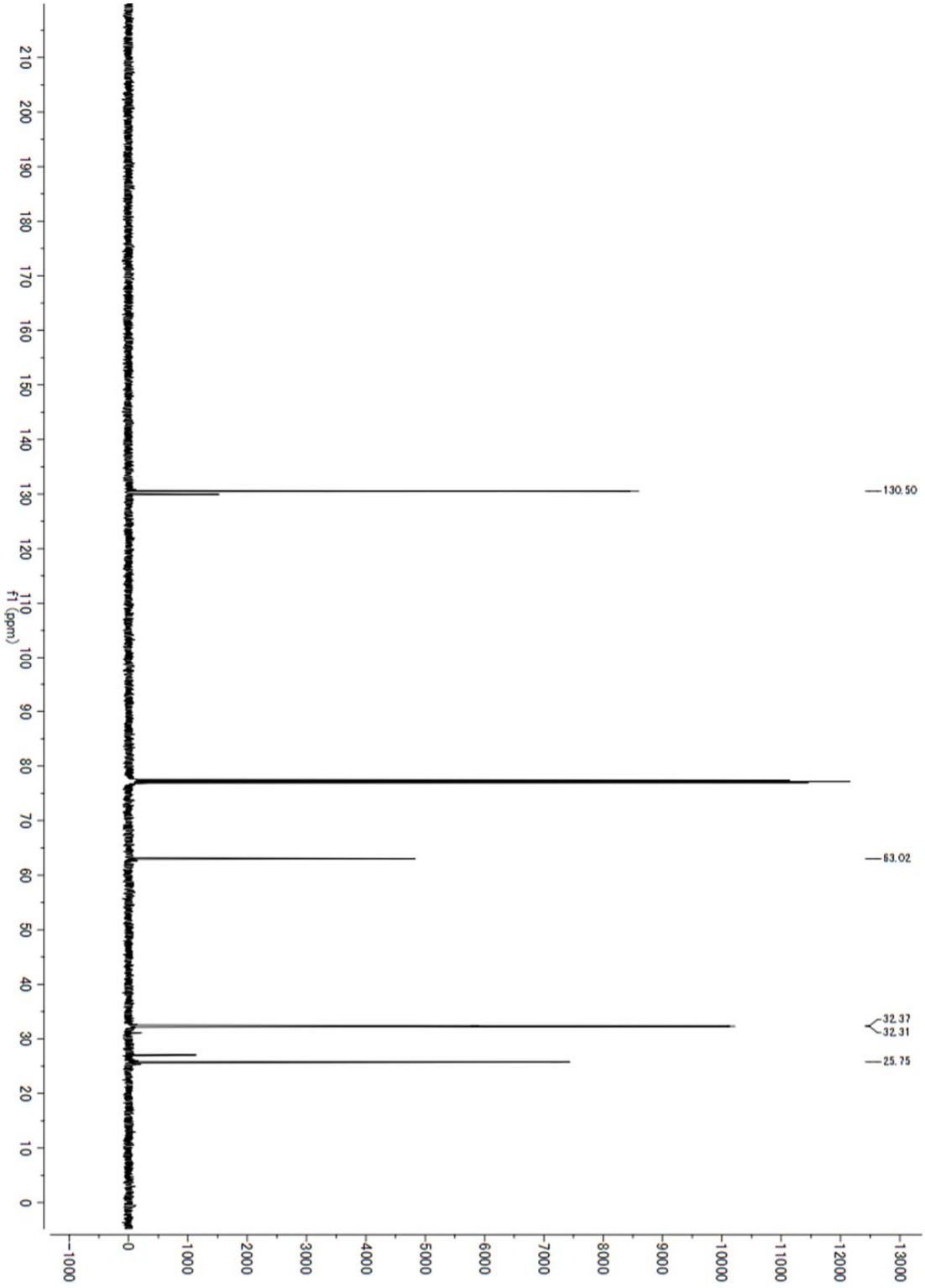


Figure 54: ^{13}C NMR (126 MHz) spectrum of **2.37** in $CDCl_3$.

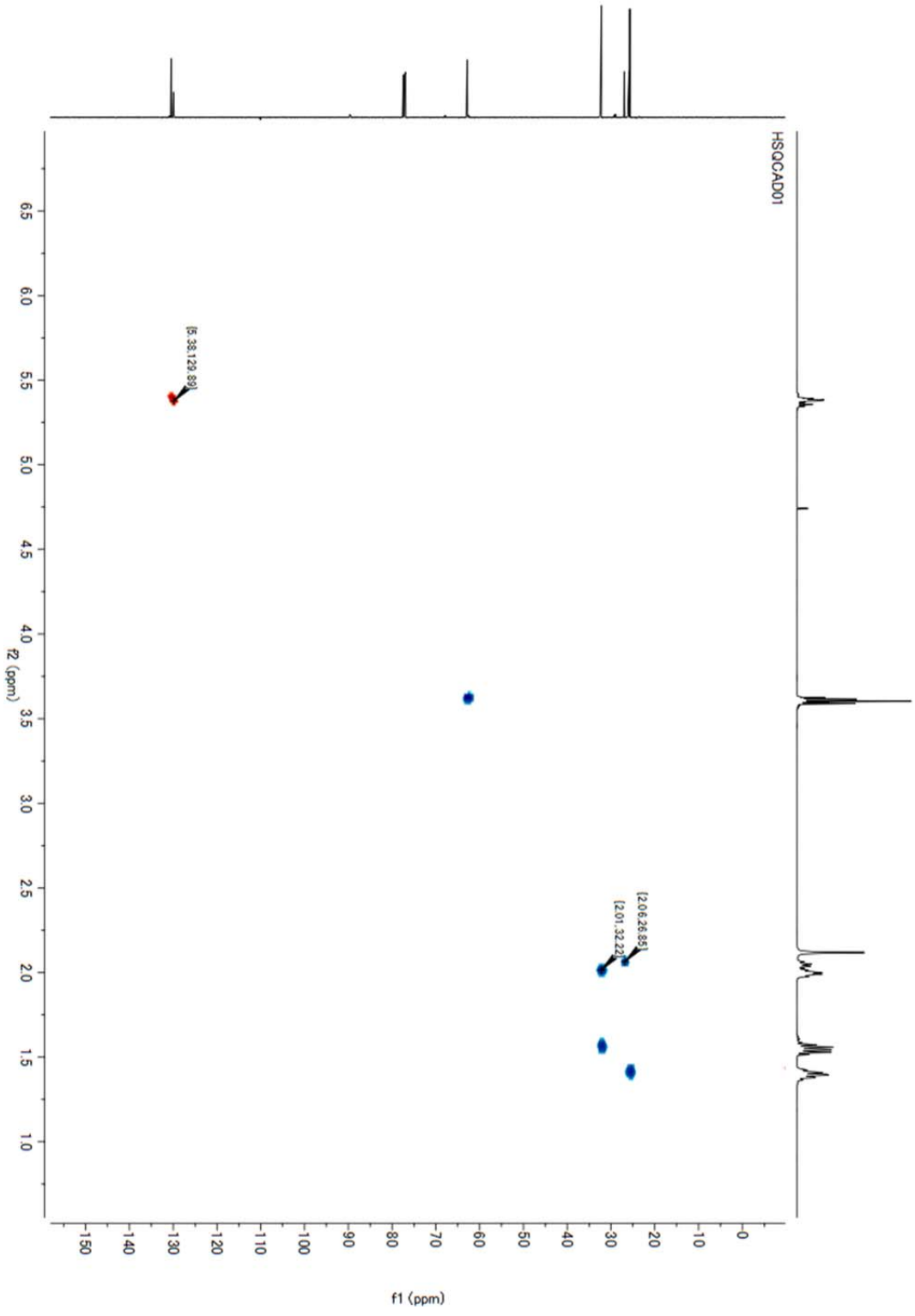


Figure 55: ^{1}H-^{13}C HSQC of **2.37** in $CDCl_3$.

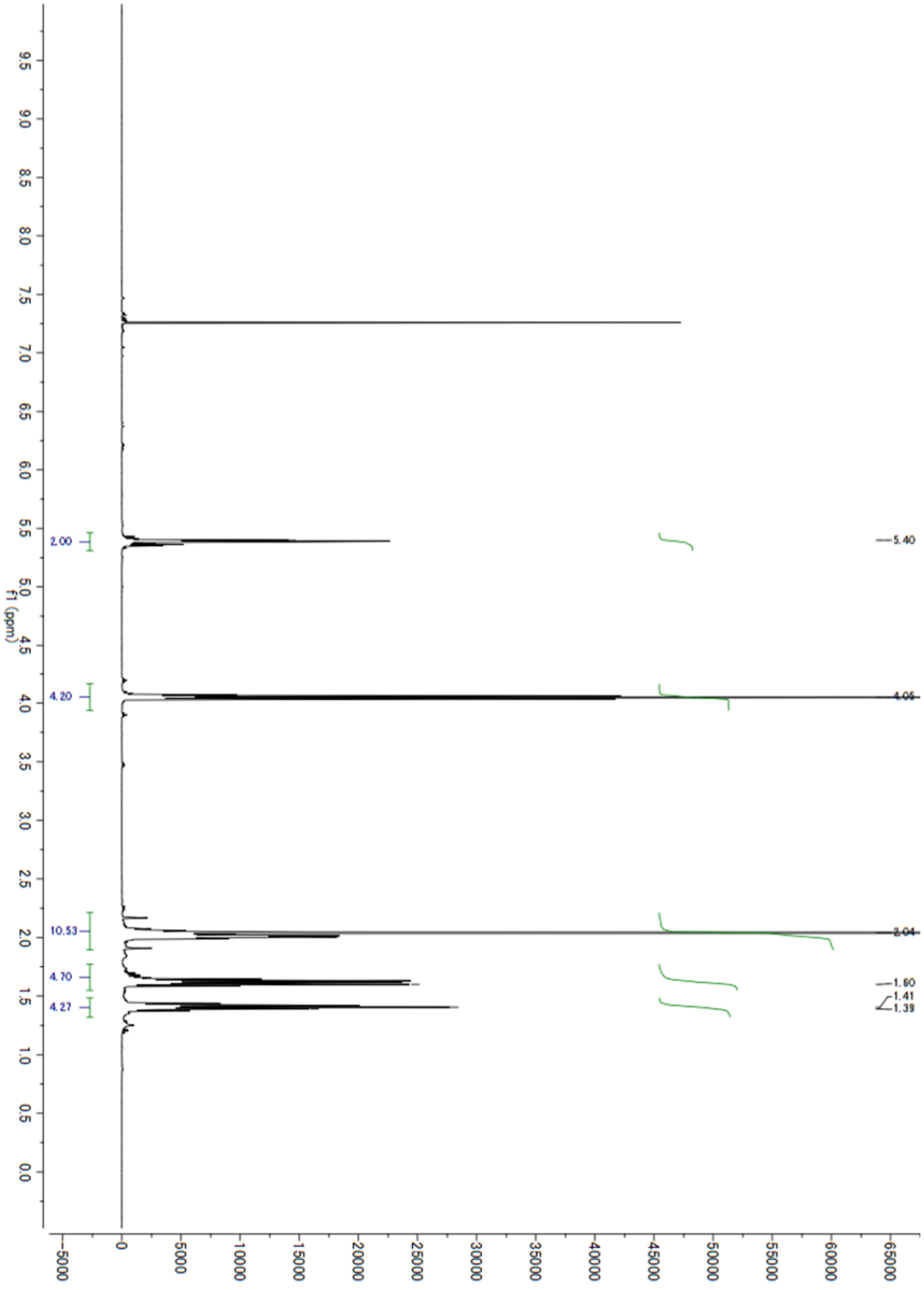


Figure 56: ^{1}H NMR (500 MHz) spectrum of **2.54** in $CDCl_3$.

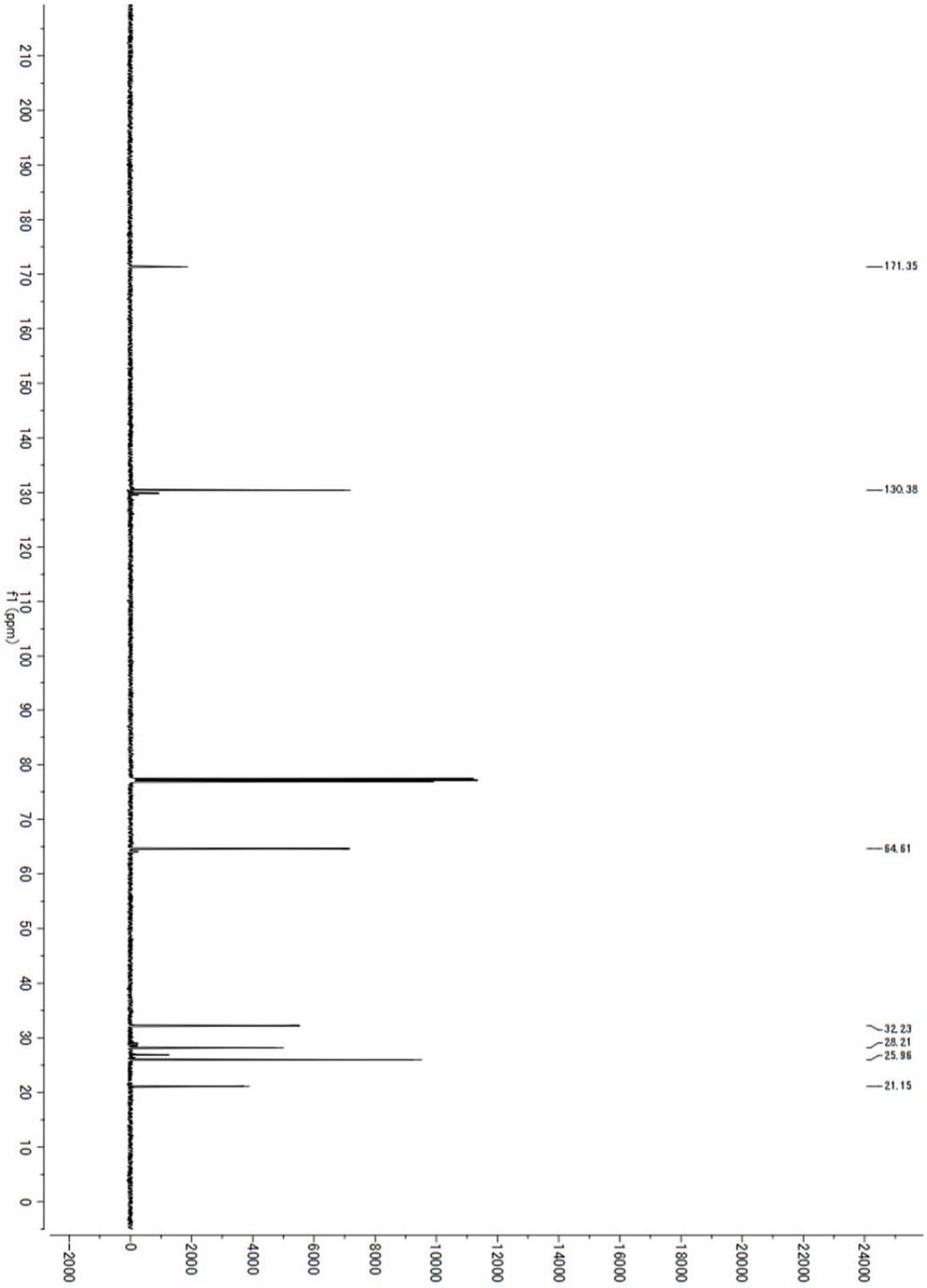


Figure 57: ^{13}C NMR (126 MHz) spectrum of **2.54** in $CDCl_3$.

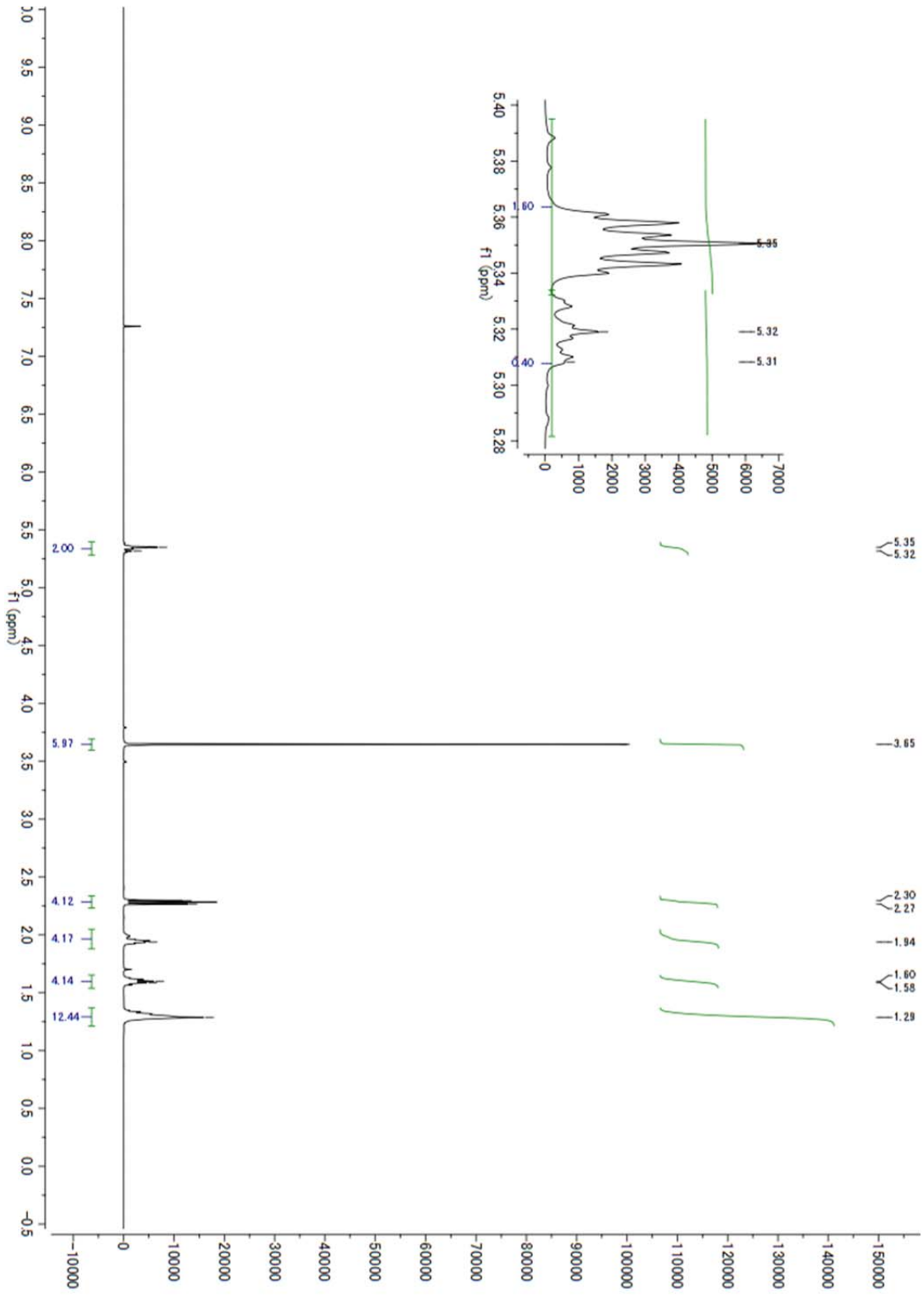


Figure 58: ^{1}H NMR (500 MHz) spectrum of **2.38** in $CDCl_3$.

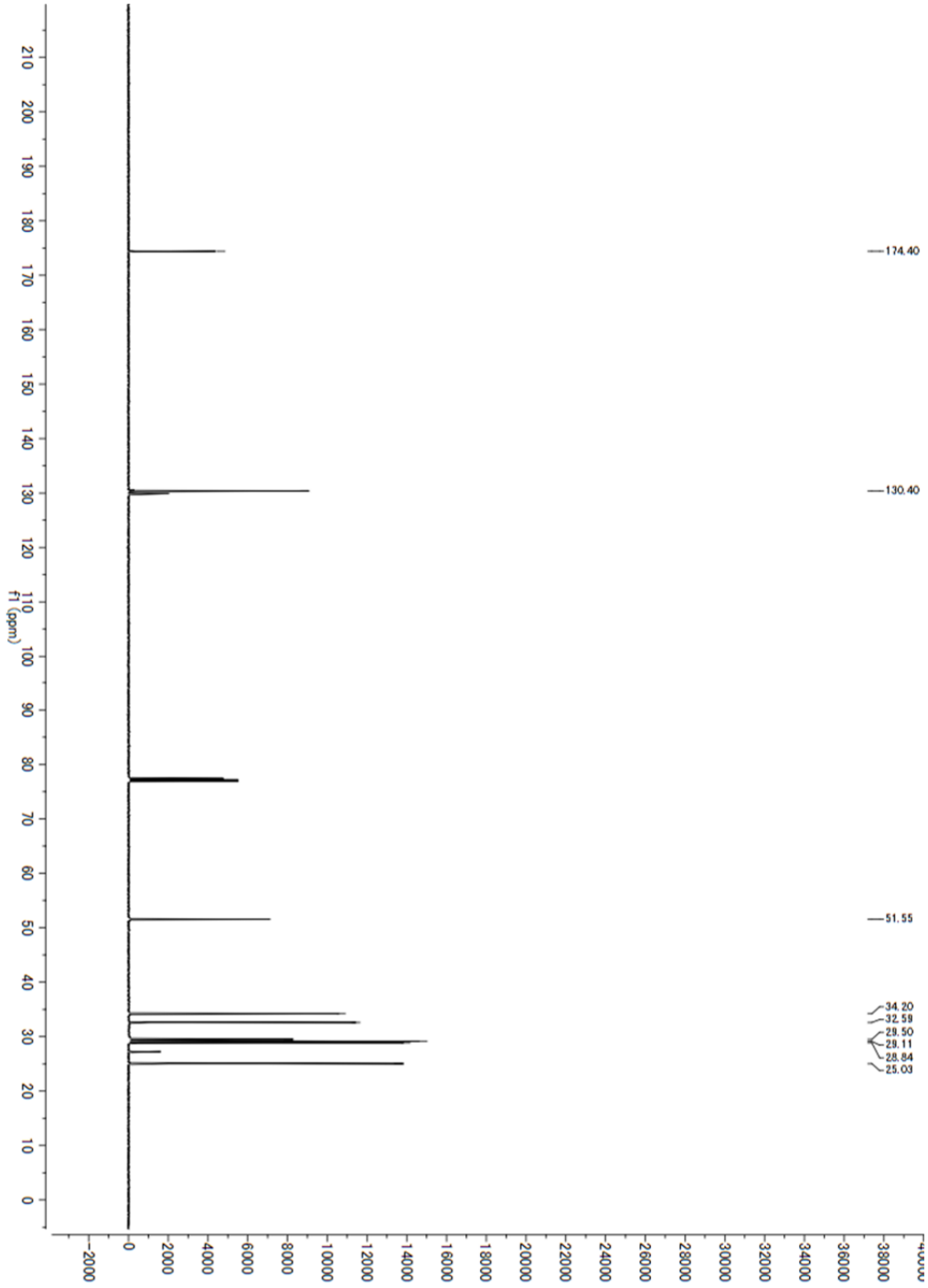


Figure 59: ^{13}C NMR (126 MHz) spectrum of **2.38** in $CDCl_3$.

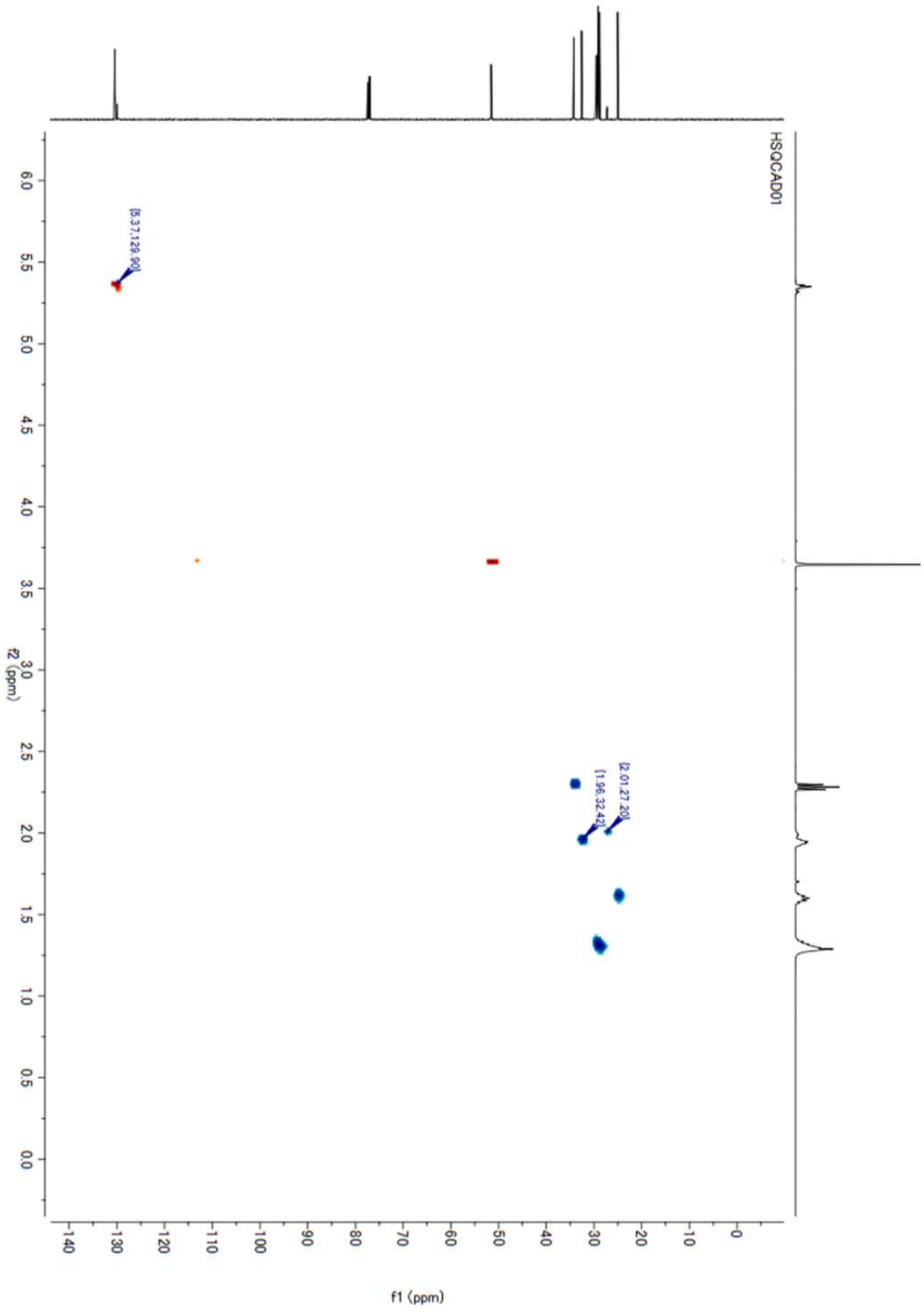


Figure 60: ^{1}H-^{13}C HSQC of **2.38** in $CDCl_3$.

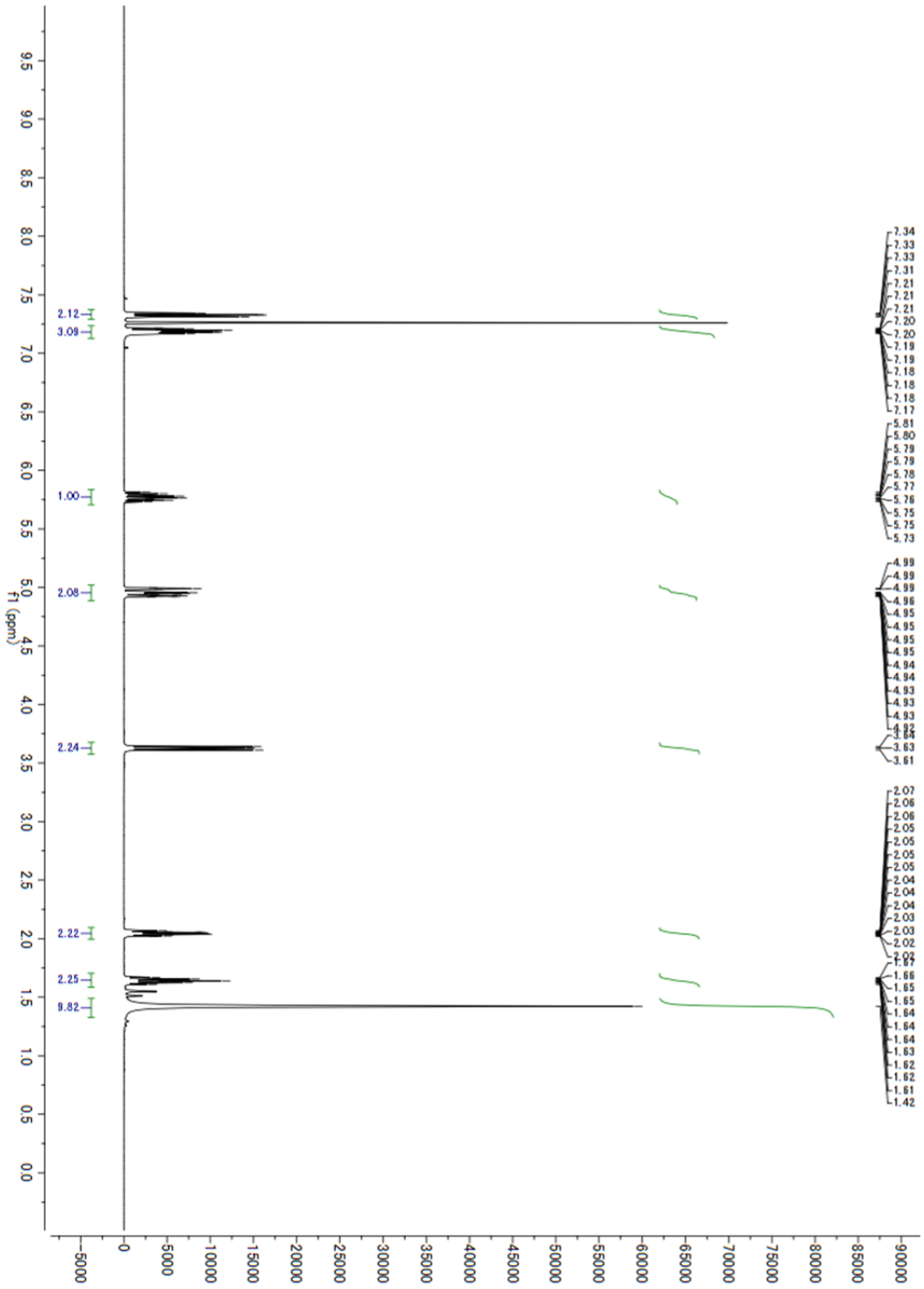


Figure 61: ^{1}H NMR (500 MHz) spectrum of **2.56** in $CDCl_3$.

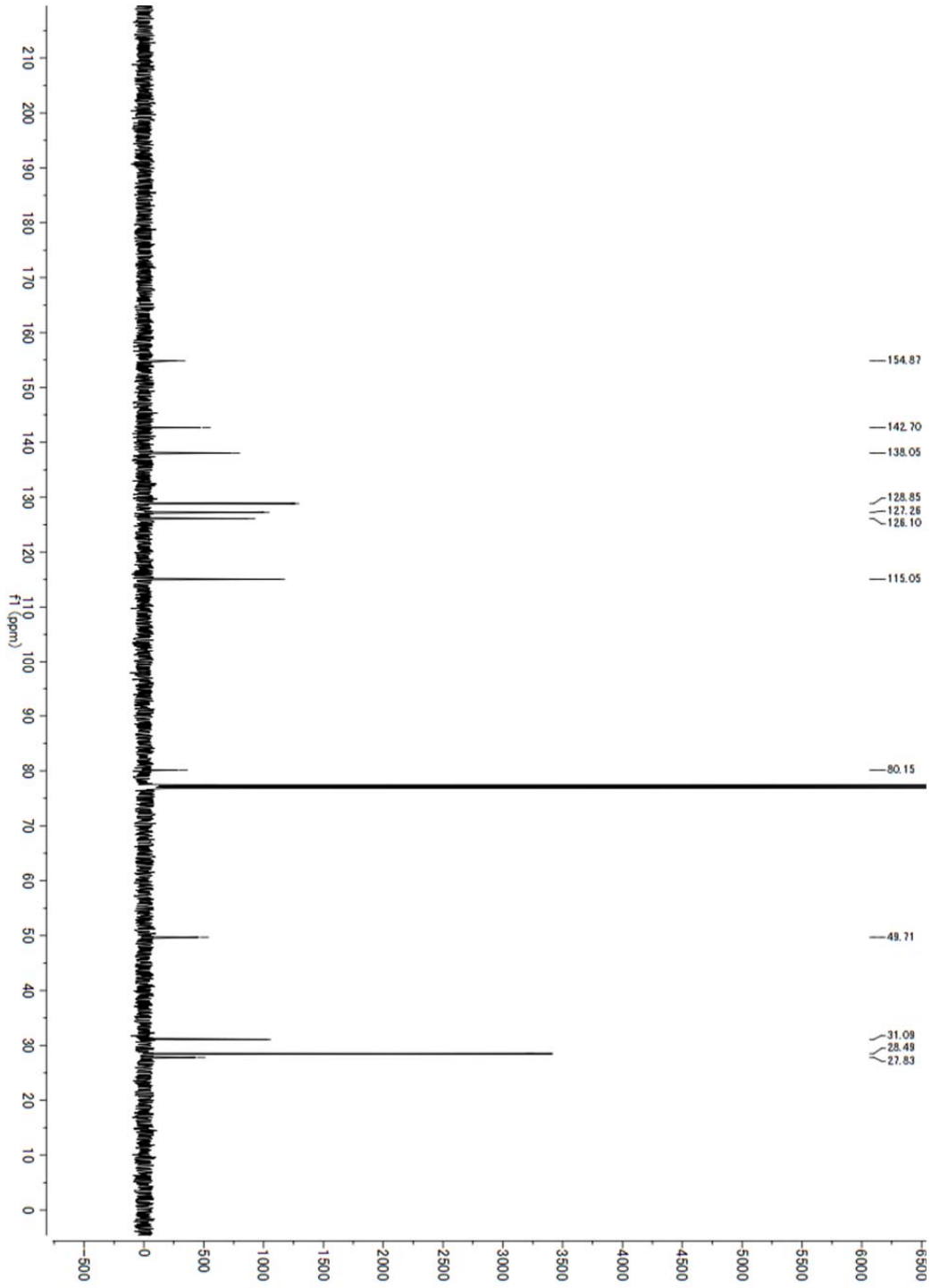


Figure 62: ^{13}C NMR (126 MHz) spectrum of **2.56** in $CDCl_3$.

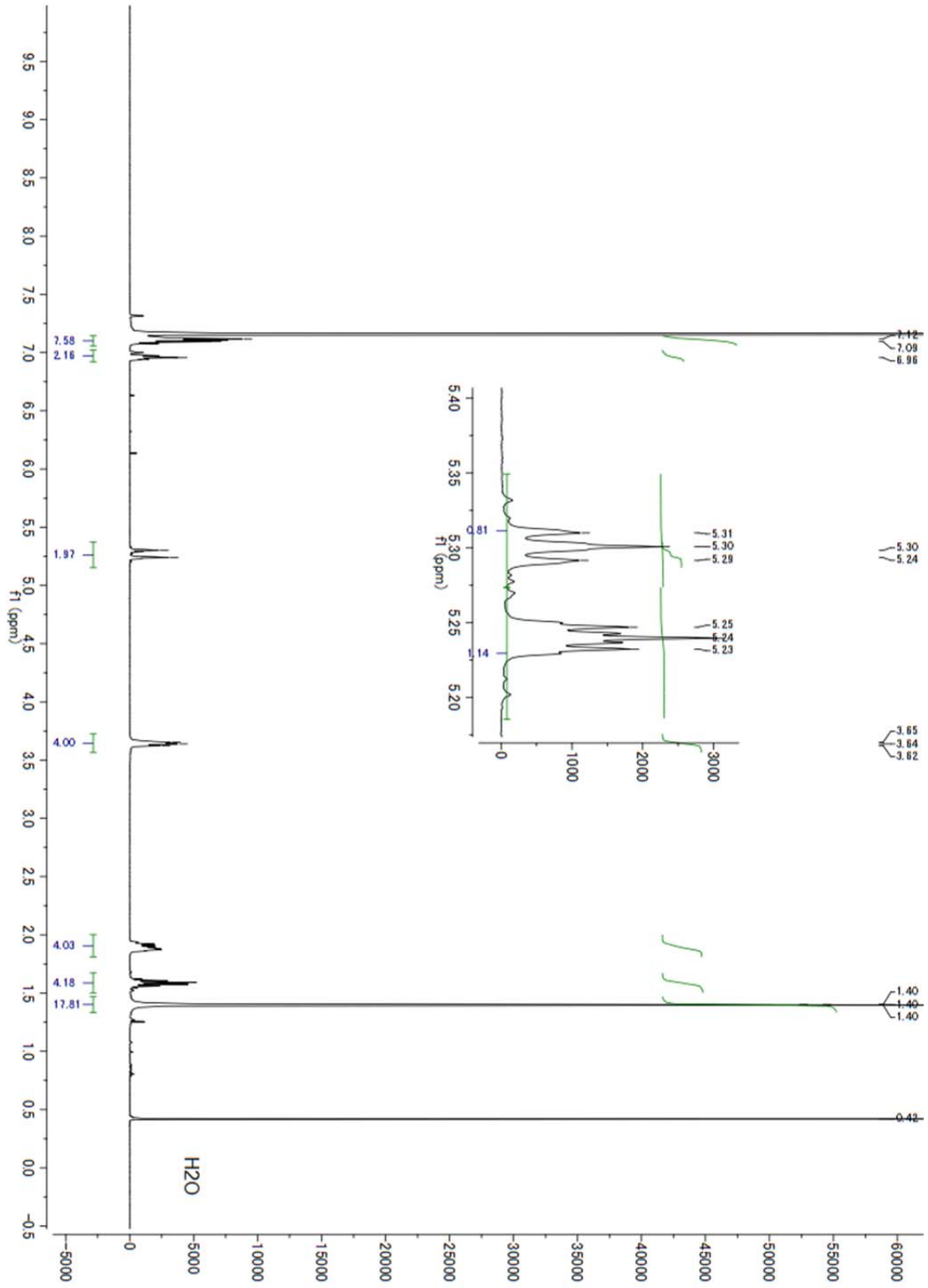


Figure 63: ^{1}H NMR (500 MHz) spectrum of **2.57** in C_6D_6.

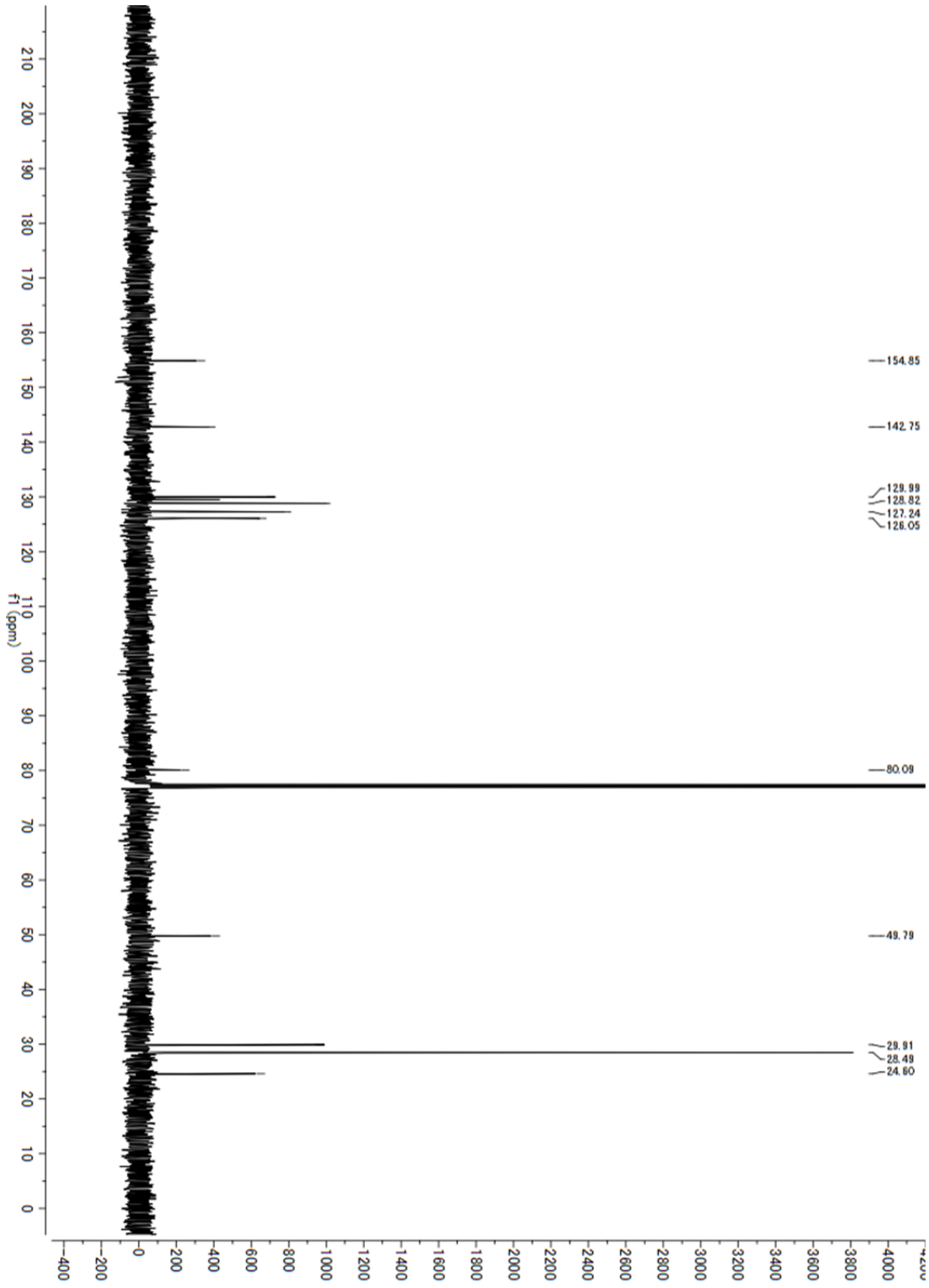


Figure 64: ^{13}C NMR (126 MHz) spectrum of **2.57** in $CDCl_3$.

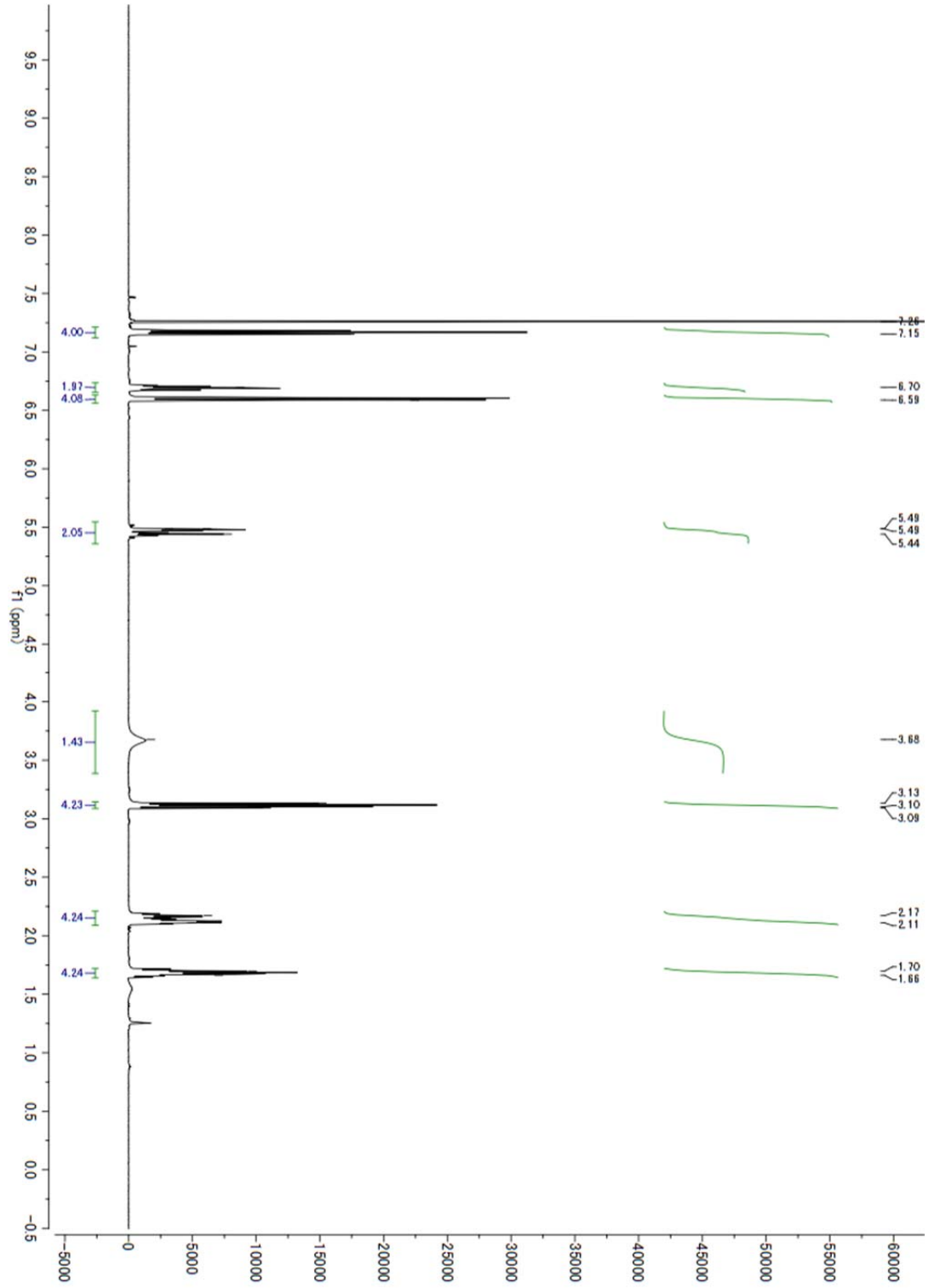


Figure 65: ^{1}H NMR (500 MHz) spectrum of **2.39** in $CDCl_3$.

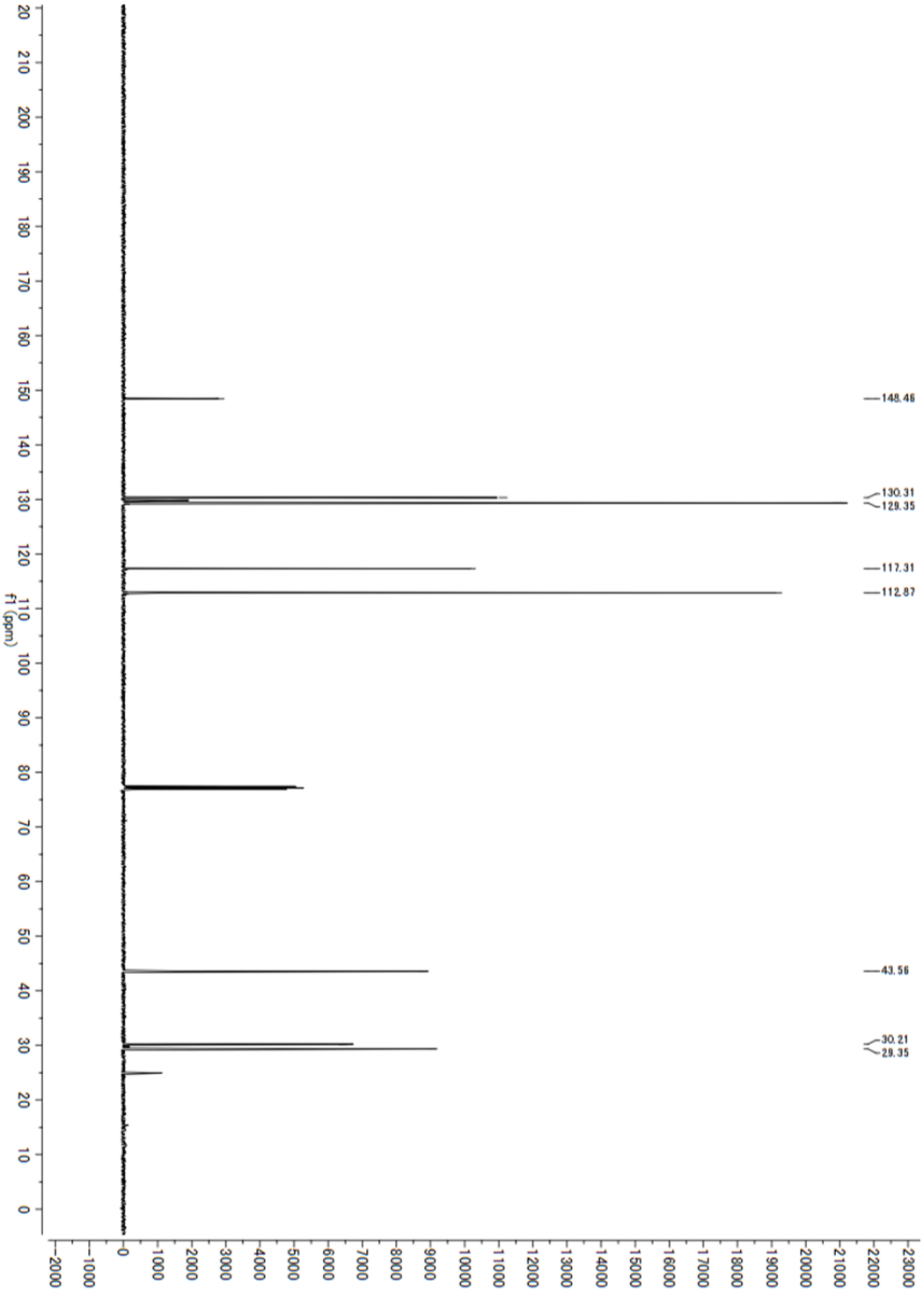


Figure 66: ^{13}C NMR (126 MHz) spectrum of **2.39** in $CDCl_3$.

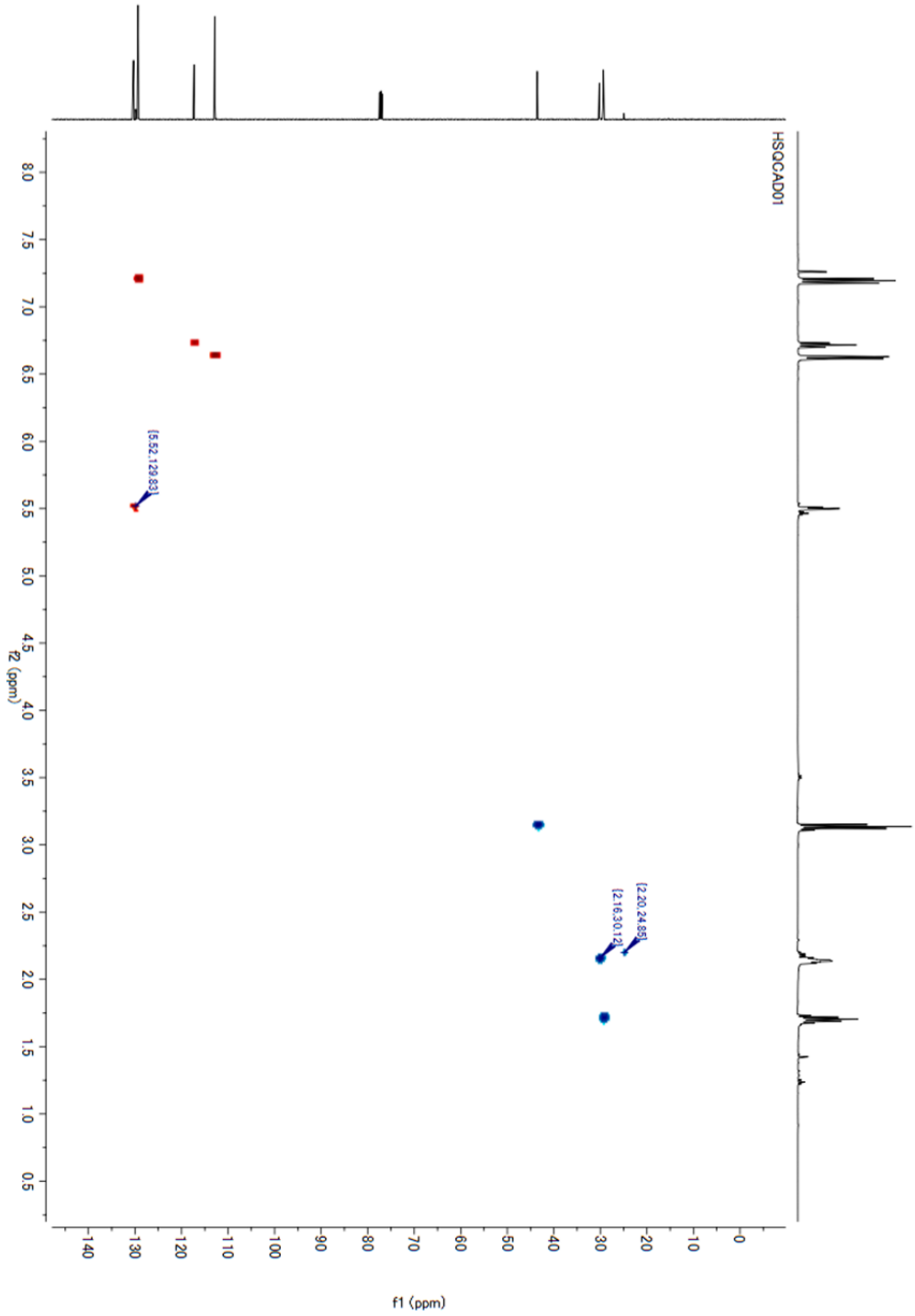


Figure 67: ^{1}H-^{13}C HSQC of **2.39** in $CDCl_3$.

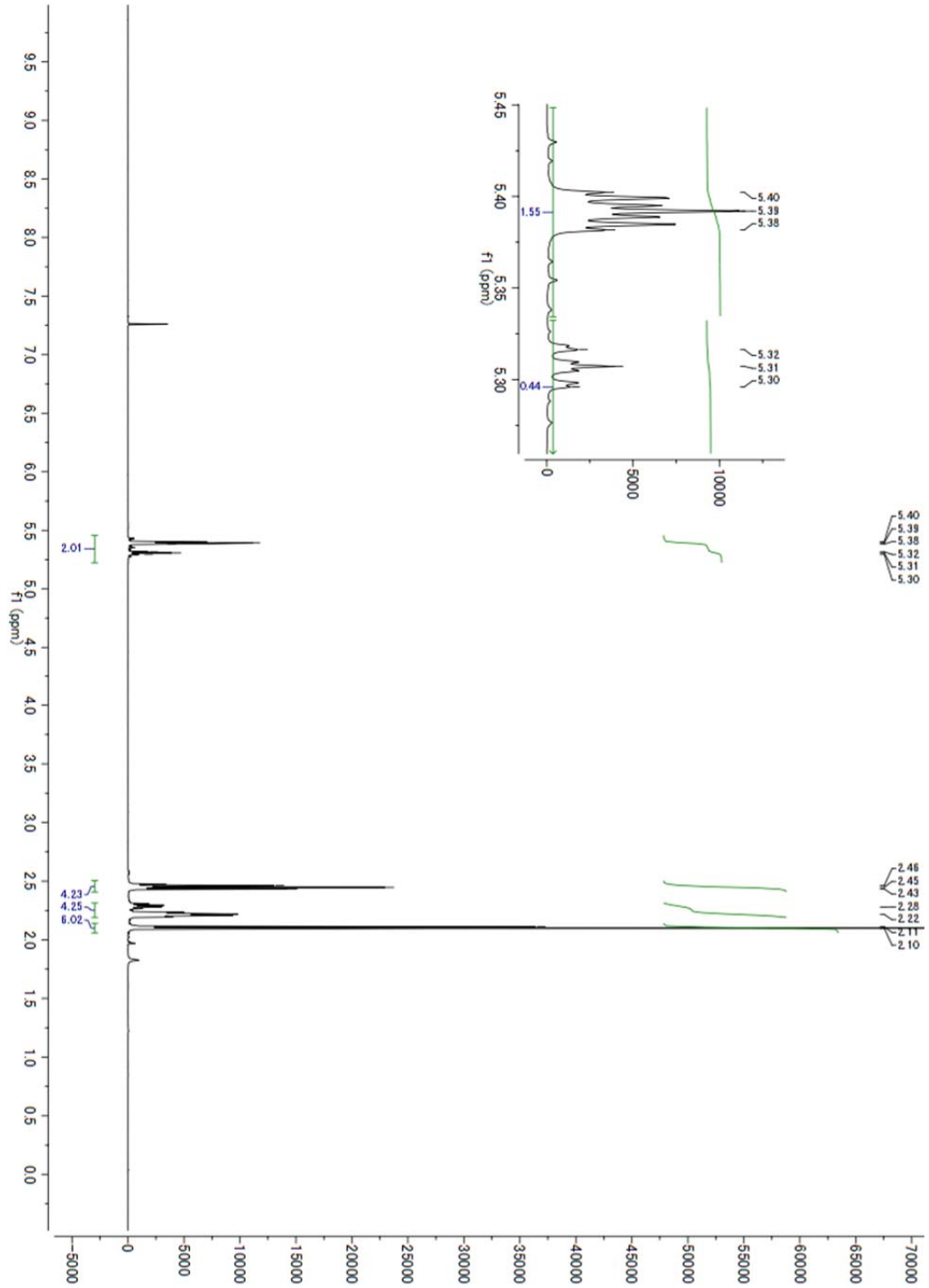


Figure 68: ^{1}H NMR (500 MHz) spectrum of **2.40** in $CDCl_3$.

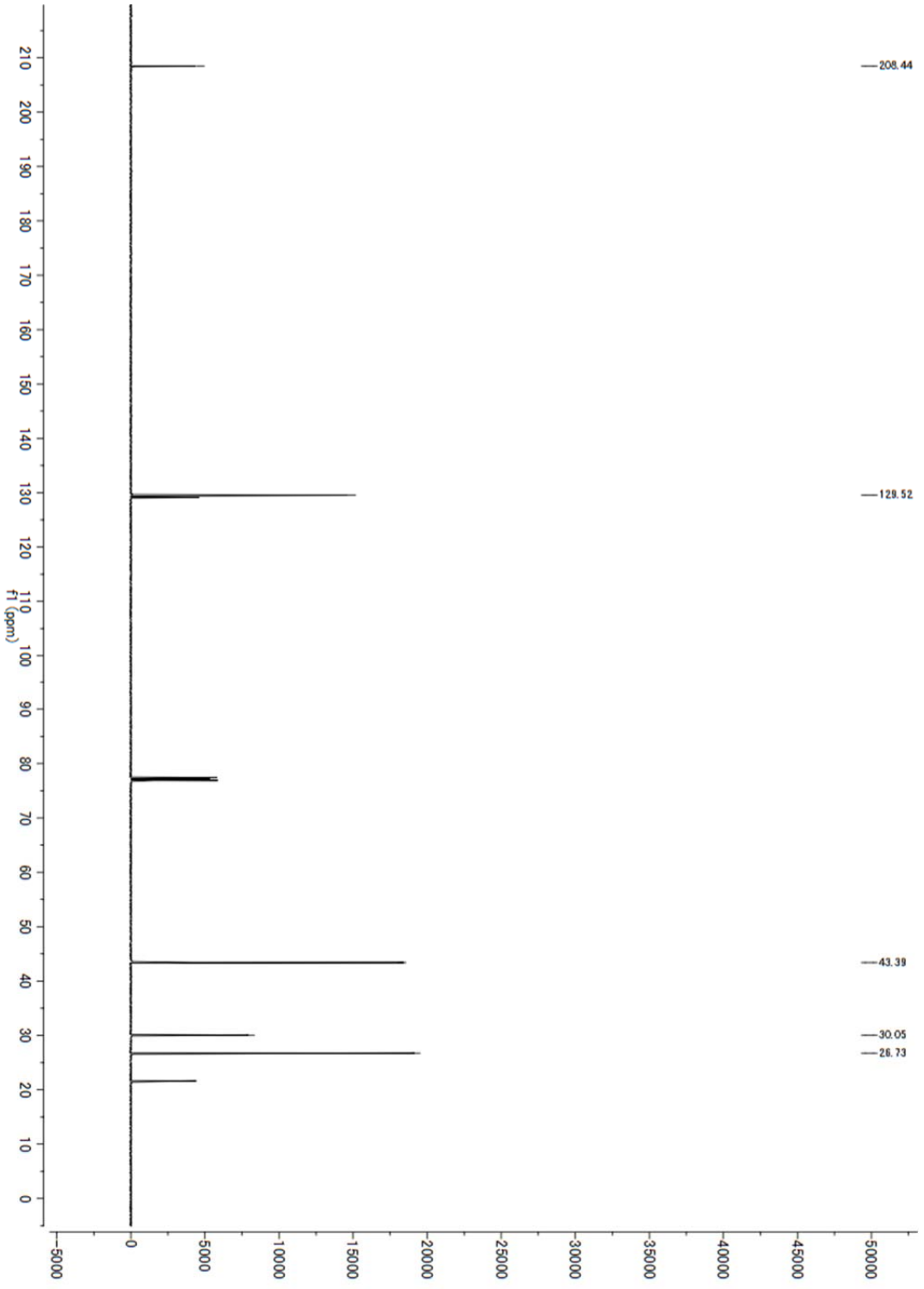


Figure 69: ^{13}C NMR (126 MHz) spectrum of **2.40** in $CDCl_3$.

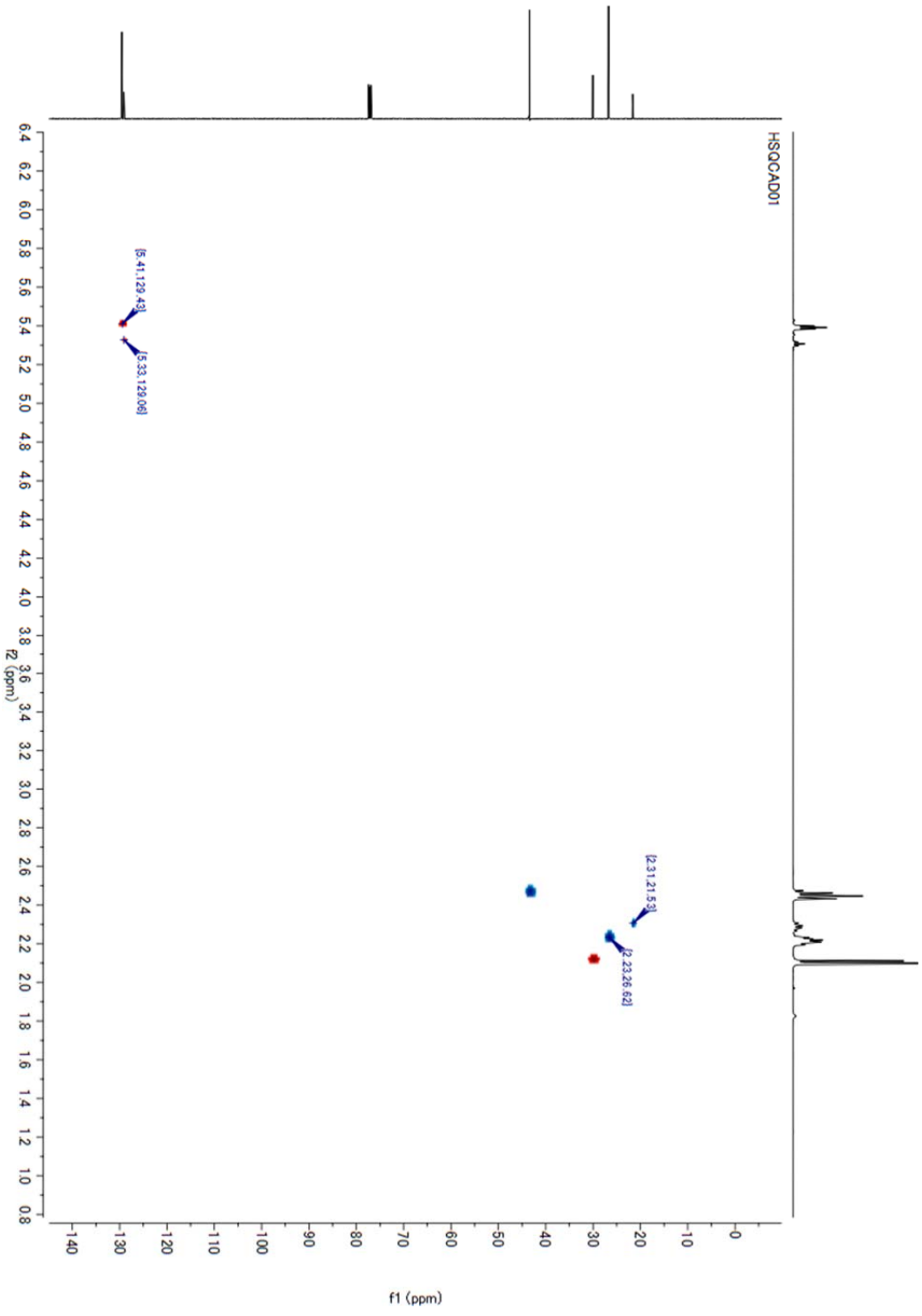


Figure 70: ^{1}H-^{13}C HSQC of **2.40** in $CDCl_3$.

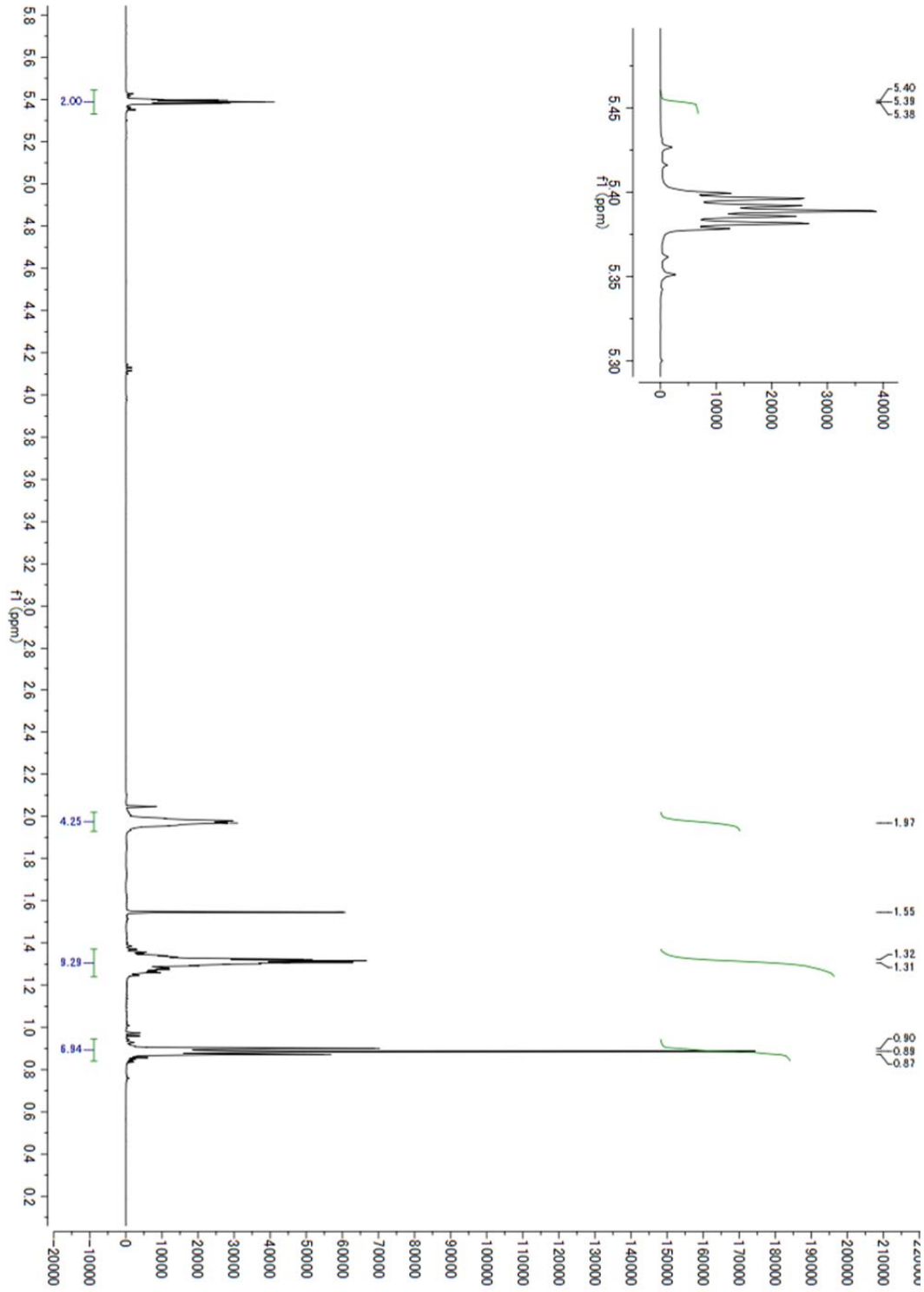


Figure 71: ^{1}H NMR (500 MHz) spectrum of the purely *E*-isomer of **2.36** in $CDCl_3$.

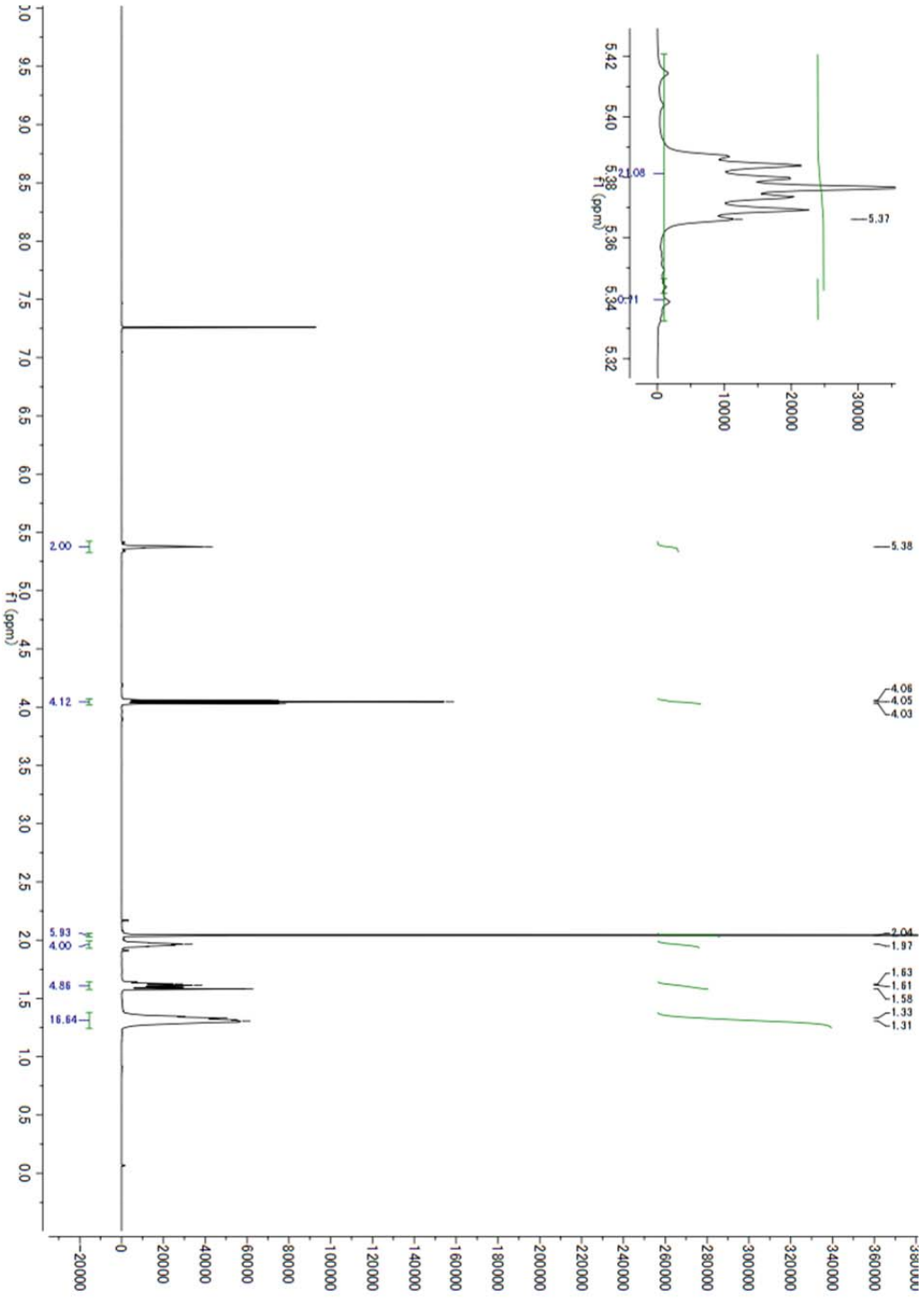


Figure 72: ^{1}H NMR (500 MHz) spectrum of the purely *E*-isomer of **2.34** in $CDCl_3$.

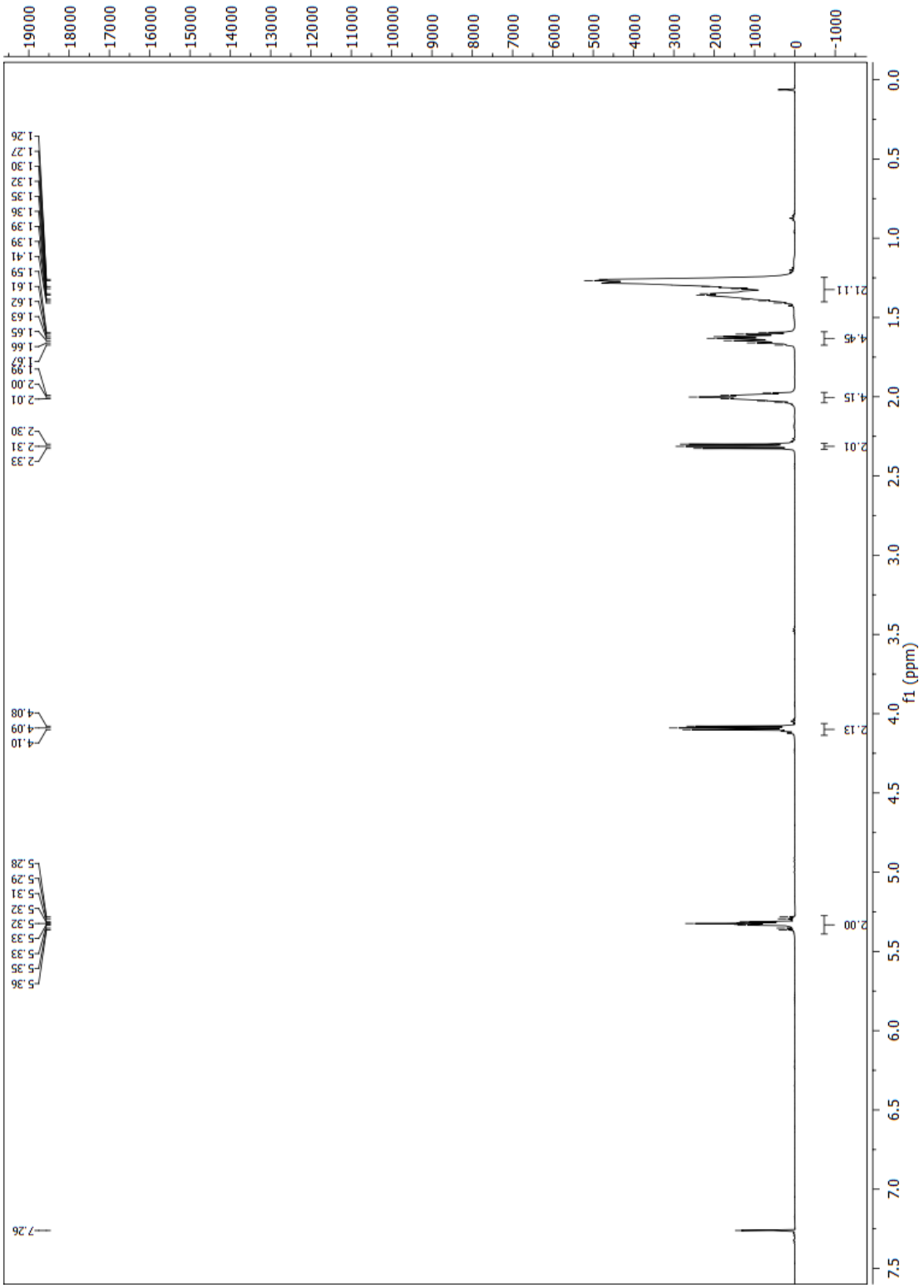


Figure 73: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *E*-oxacycloicos-11-en-2-one (**2.41**).

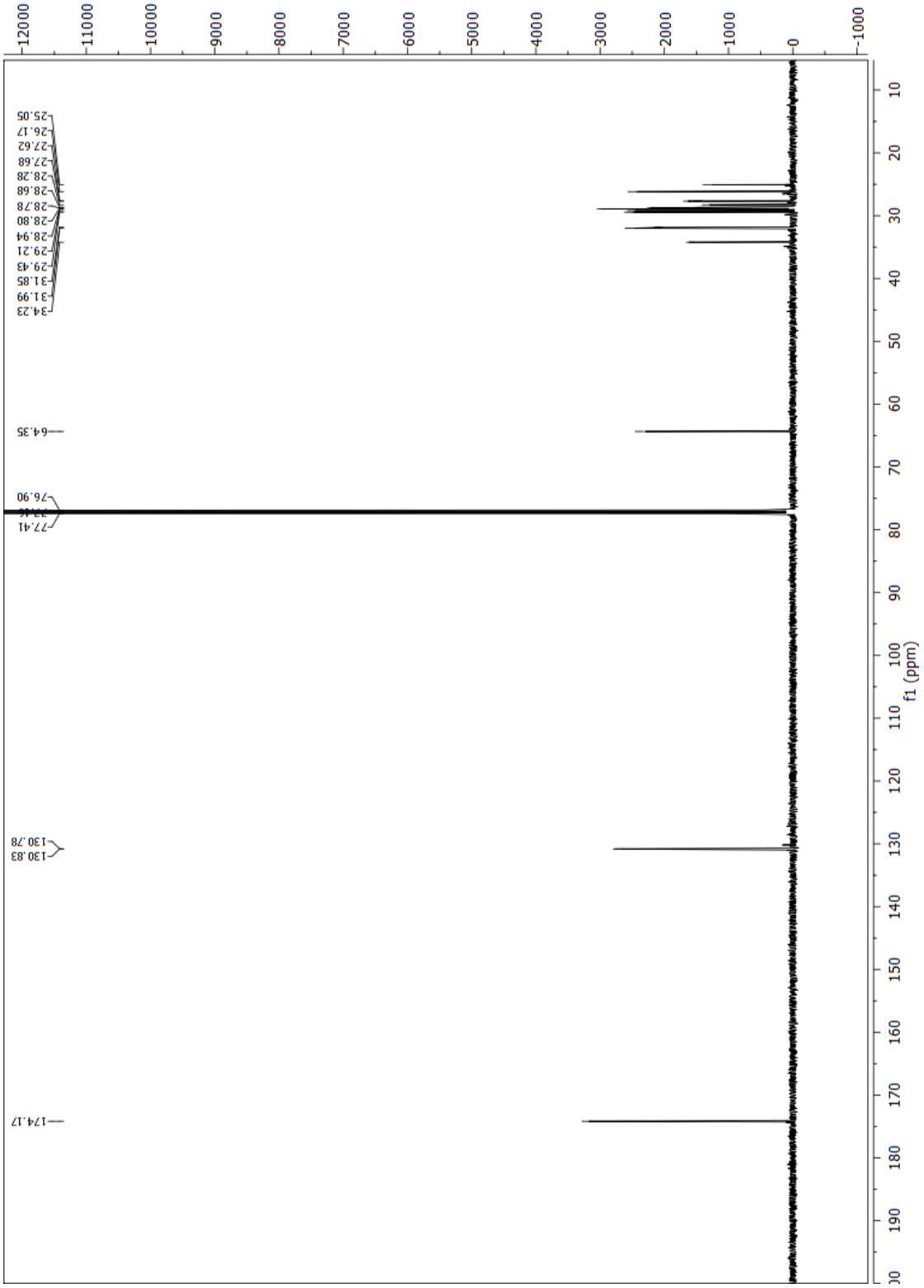


Figure 74: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *E*-oxacycloicos-11-en-2-one (**2.41**).

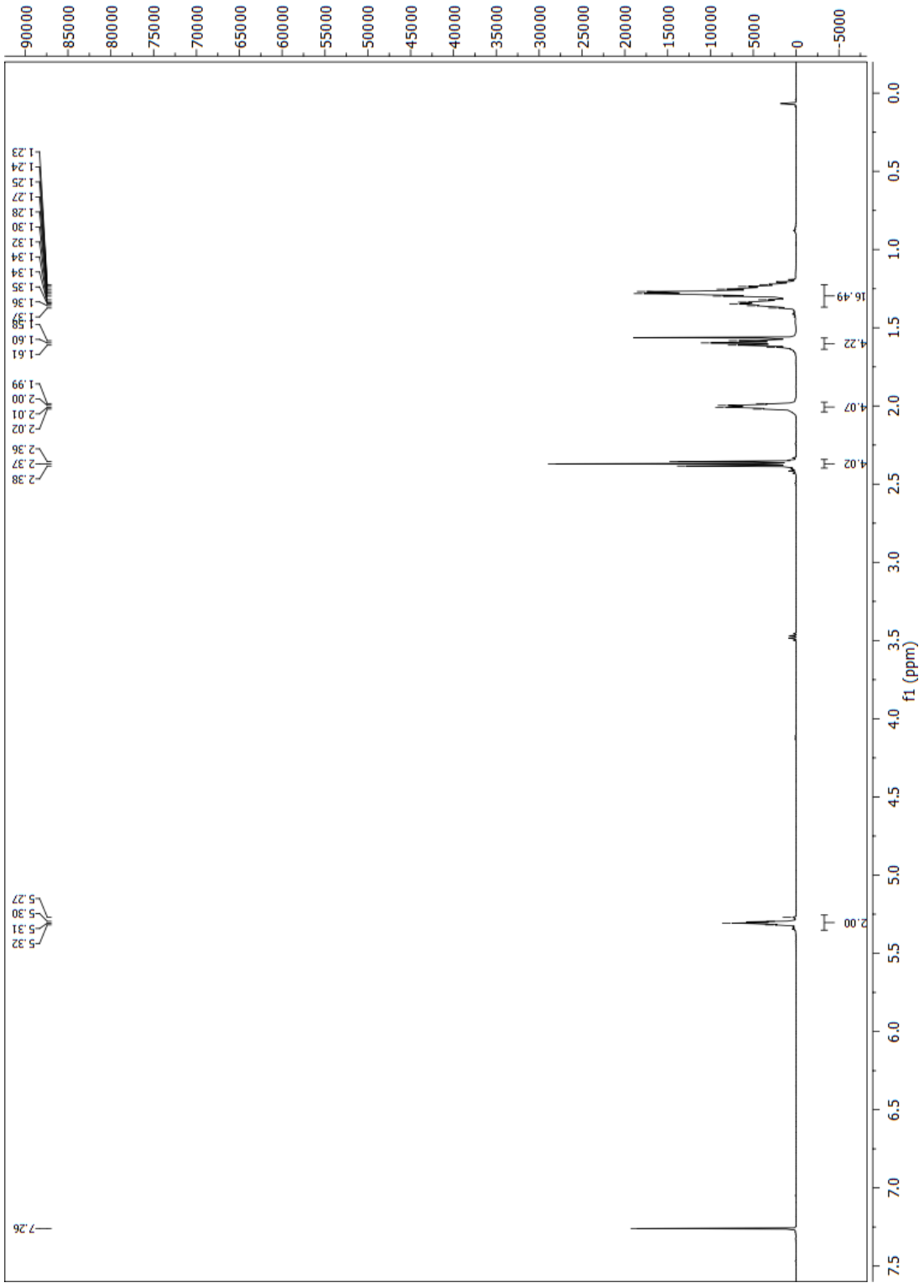


Figure 75: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *E*-cycloheptadec-9-enone (**2.42**).

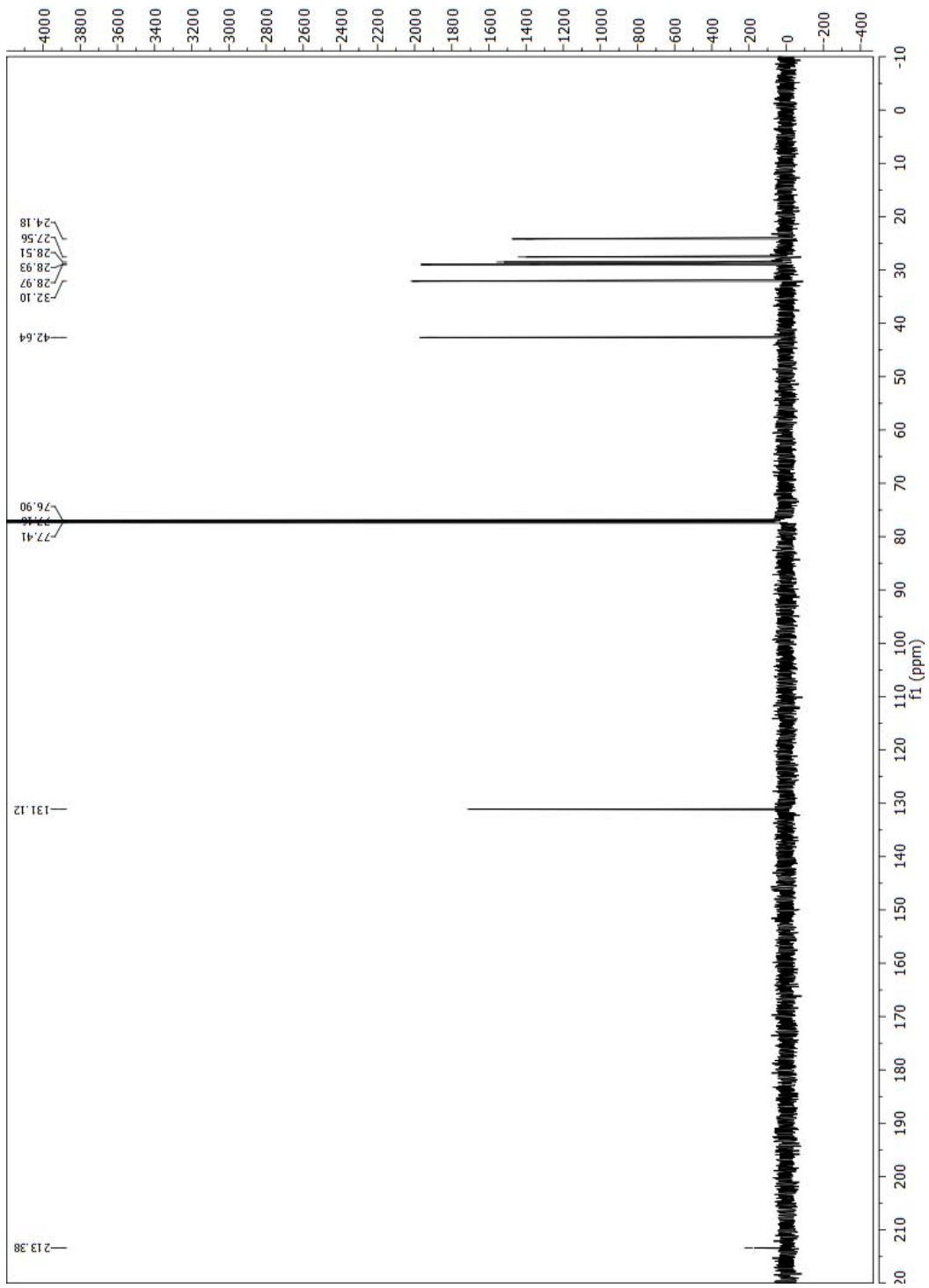


Figure 76: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *E*-cycloheptadec-9-enone (**2.42**).

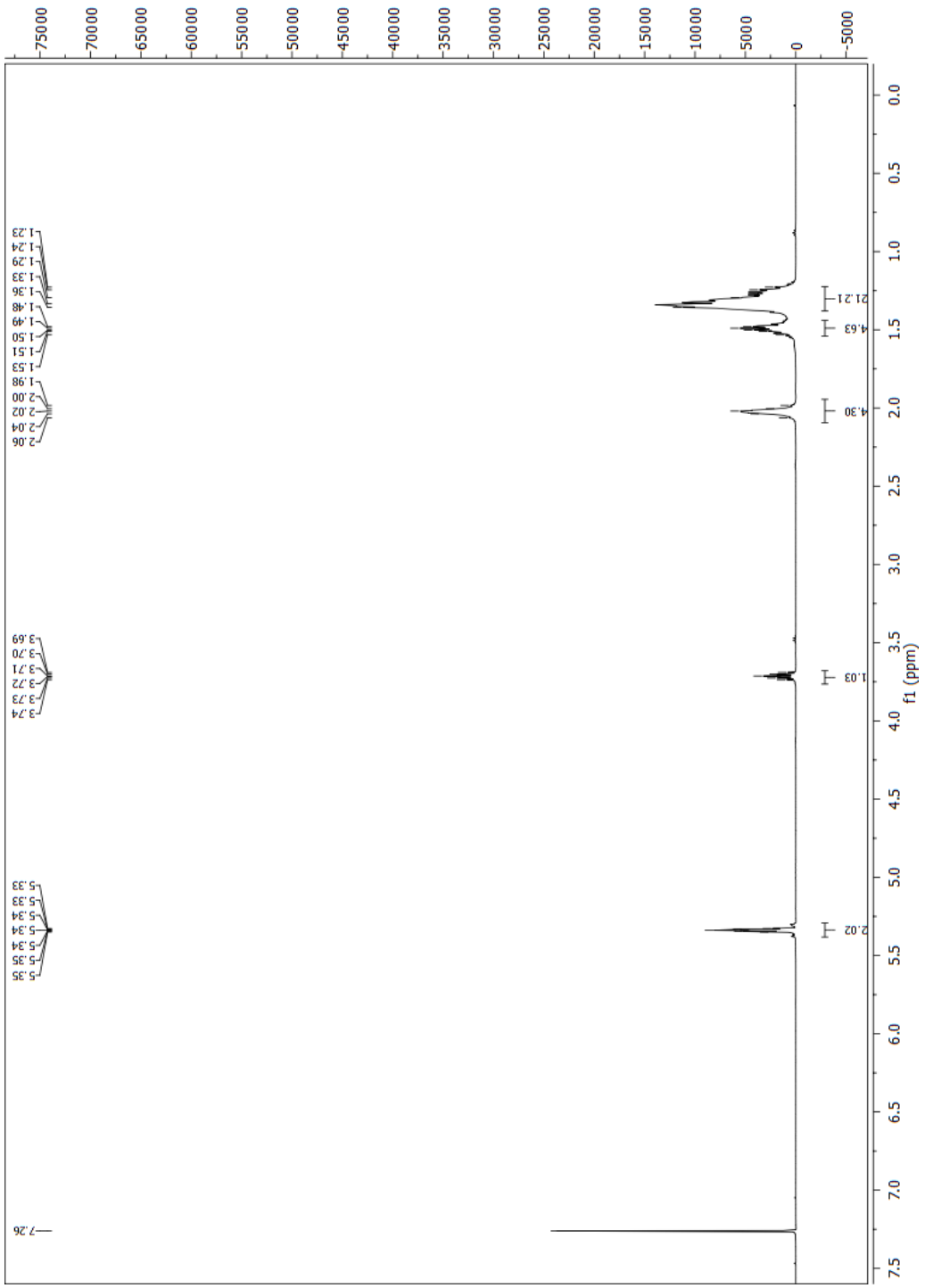


Figure 77: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *E*-cycloheptadec-9-enol (**2.43**).

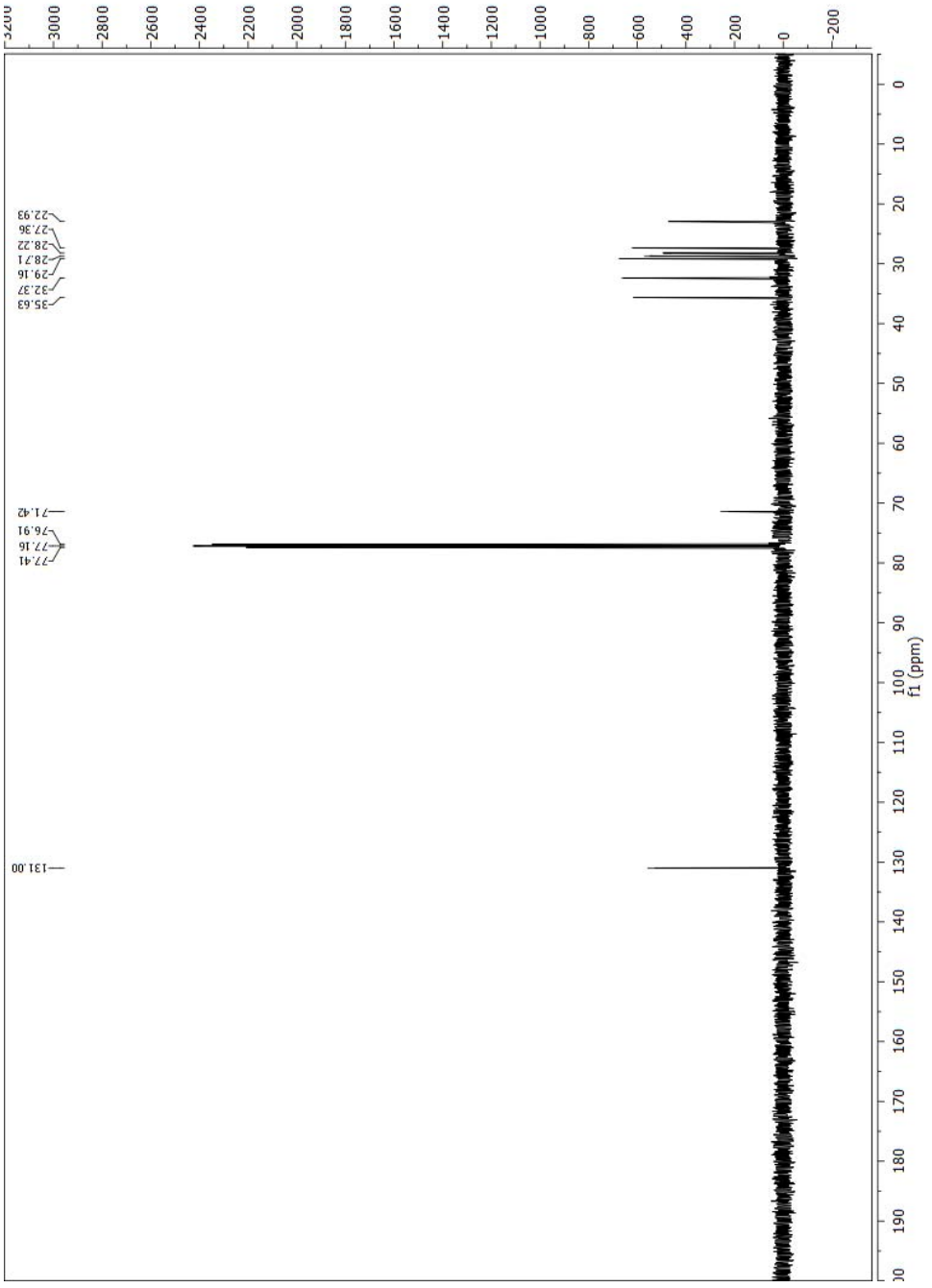


Figure 78: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *E*-cycloheptadec-9-enol (**2.43**).

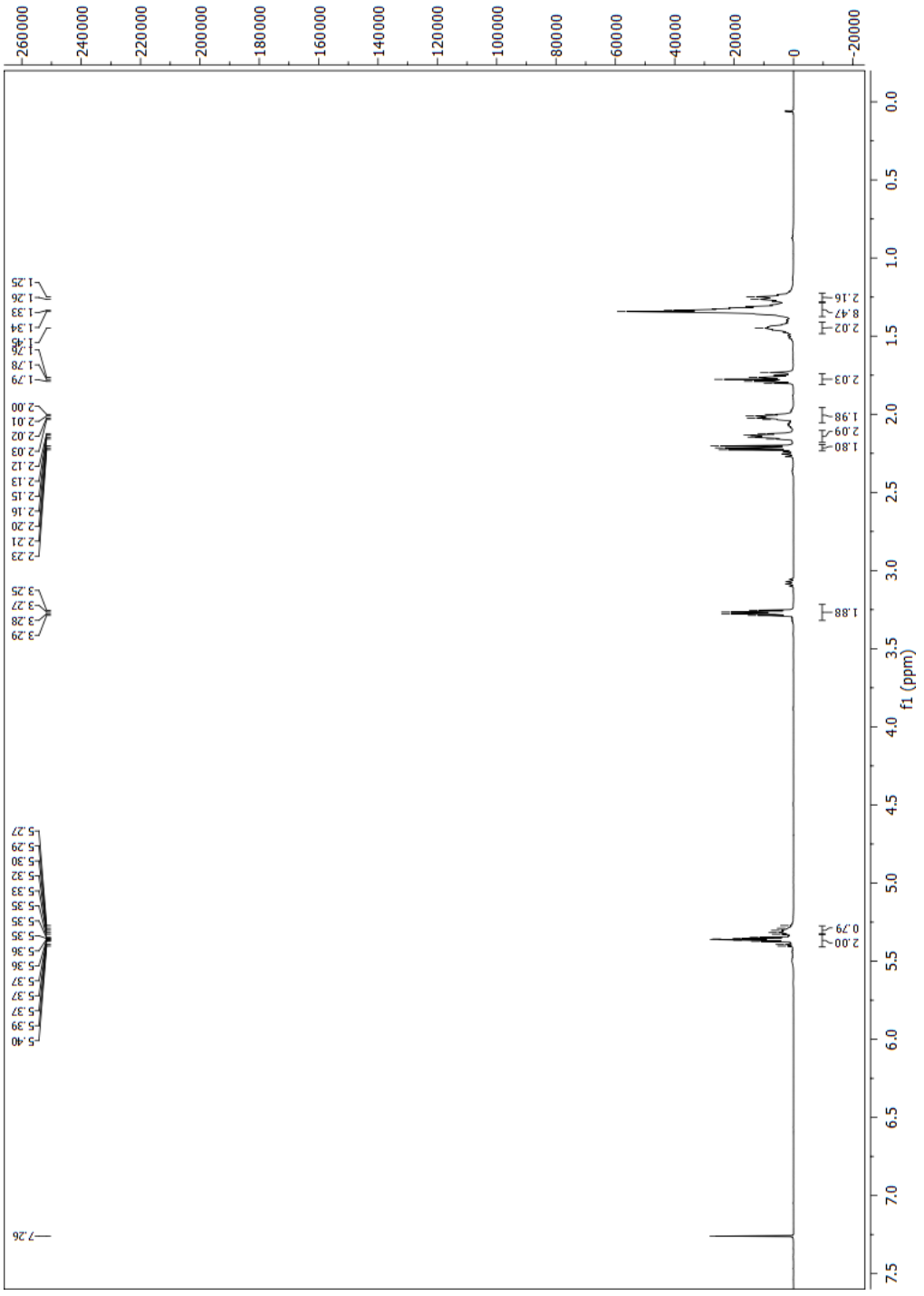


Figure 79: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *E*-azacyclopentadec-6-en-2-one (**2.44**).

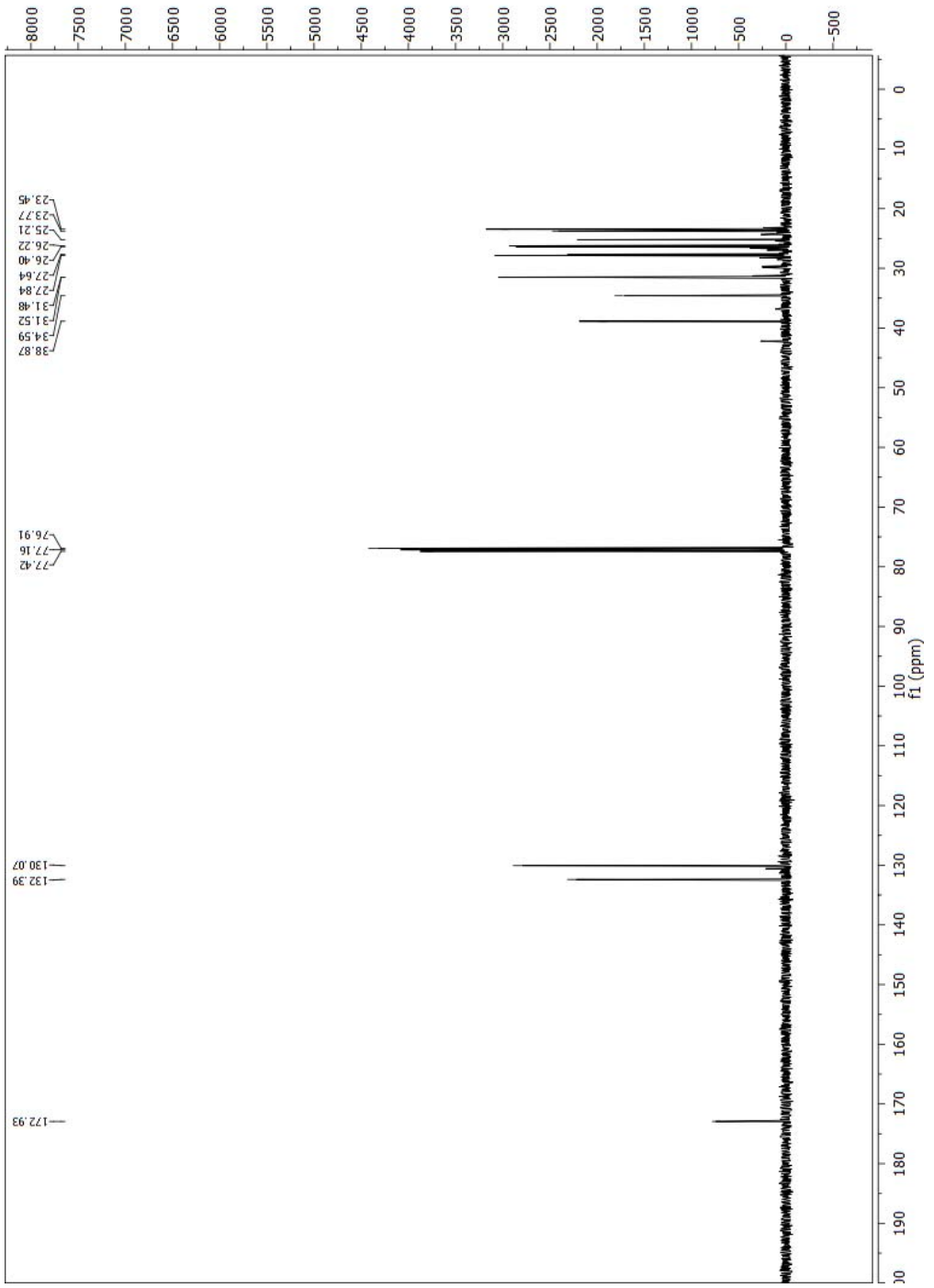


Figure 80: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *E*-azacyclopentadec-6-en-2-one (**2.44**).

C h a p t e r 3

MECHANISTIC INVESTIGATIONS OF HIGHLY *Z*-SELECTIVE RUTHENIUM ALKYLIDENE CATALYSTS

ABSTRACT:

In order to design improved catalysts and expand the substrate scope of *Z*-selective olefin metathesis transformations, the mechanism of reactions catalyzed by NHC-chelated complexes was explored. It became evident that these catalysts proceed through a mechanism distinct from previous generations of ruthenium alkylidene catalysts. Using density functional theory calculations, the stability of differentially substituted metallacyclobutane intermediates was used to explain experimental observations. In particular, it was calculated that the formation of trisubstituted metallacycles with NHC-chelated catalysts was highly unfavorable, which helped explain the observation that internal olefins cannot react with each other in a productive manner. Additionally, it seems that productive cross metathesis reactions generally proceed through 1,2-disubstituted metallacyclobutanes that are relevant to the *Z*-selective ethenolysis reactivity of our family of catalysts. More recent investigations were aimed at determining if the *Z*-selective ethenolysis reactivity of NHC-chelated catalysts could have implications for observed *Z*-content degradation.

MECHANISTIC IMPLICATIONS OF *Z*-SELECTIVE ETHENOLYSIS:

Following up on our initial observations that **3.1** was a highly effective *Z*-selective ethenolysis catalyst (see Chapter 2), we attempted to quantify its ethenolysis selectivity by investigating the relative rates of degradation of *E* and *Z* internal olefins using ^{1}H NMR spectroscopy (Figure 1). 5-Decene was chosen as a substrate because the stereopure *E*- and *Z*-isomers are commercially available. The rate of ethenolysis was found to be first-order in substrate[1] and the relative rates of 5-decene ethenolysis were determined at 1 atm of ethylene. Neither the ethenolysis of *Z*-5-decene nor *E*-5-decene proceeded to completion under the reaction conditions.[2] Nevertheless, log plots of substrate concentration versus time at early reaction times

were found to be linear (*E*-5-decene, $R^2 = 0.93$, *Z*-5-decene, $R^2 = 0.98$). From the slopes of these plots, the ratio of the rate constants for ethenolysis of *Z*-5-decene and *E*-5-decene (k_Z/k_E) was found to be ~4.5. The corresponding k_Z/k_E value reported for molybdenum catalyst **3.5**, 30 ± 5, is significantly higher, implying that catalyst **3.5** is inherently more selective than **3.1**. The functional group tolerance of catalyst **3.1** and the *Z*-selectivity at ethylene pressures as low as 1 atm highlights advantages of this particular ruthenium-based system for the preparation of terminal olefins from internal olefins and for the purification of *Z*/*E* mixtures.[3] The further development of chelated catalysts with increased *Z*-selectivity, like catalyst **3.2**, will likely lead to increased k_Z/k_E values.

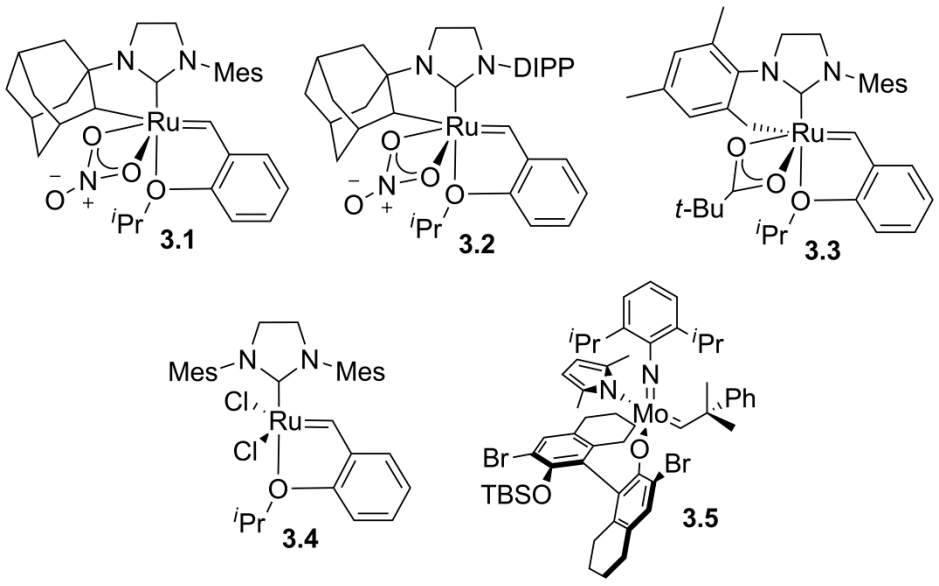


Figure 1: Previously reported olefin metathesis catalysts.

Ethenolysis Computational Investigations

In order to understand the mechanism of ethenolysis and the origin of *Z*-selectivity with catalyst **3.1**, we computed the ethenolysis reaction pathways and the *Z*/*E*-selectivity with density functional theory (DFT). The calculations were performed using Gaussian 09[4] with a theoretical

level found to be satisfactory in our previous computational studies of chelated ruthenium catalysts. Geometries were optimized in the gas phase with B3LYP[5]/LANL2DZ–6-31G(d). Single point calculations were performed with M06[6]/SDD–6-311+G(d,p) and the SMD[7] solvation model with THF solvent.

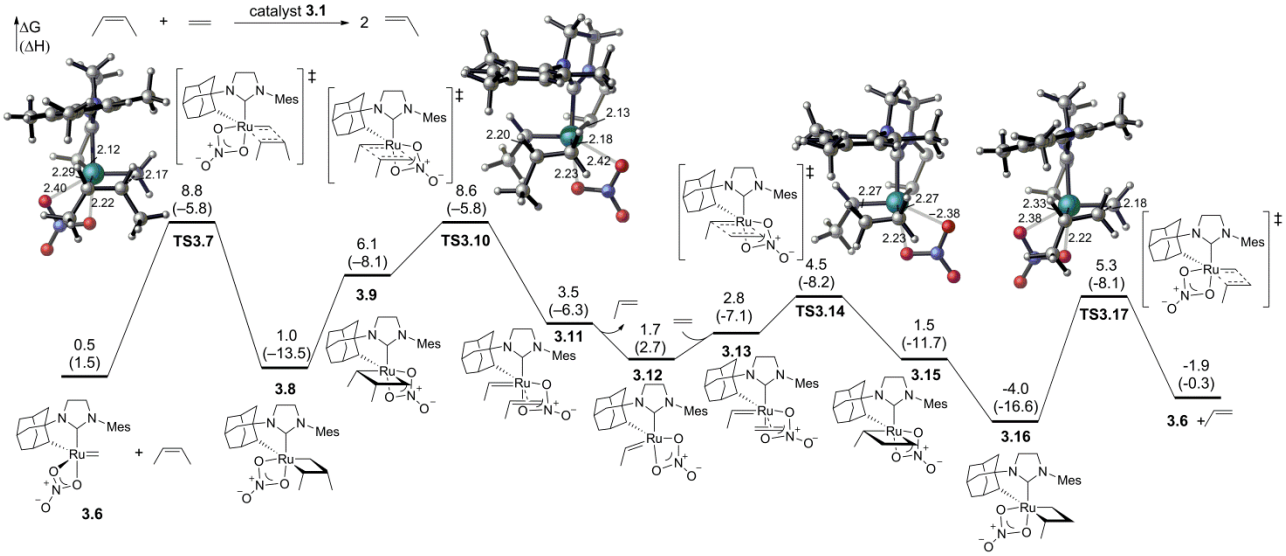


Figure 2: The most favorable pathway of ethenolysis of *cis*-2-butene with catalyst **3.1**. Gibbs free energies and enthalpies (in parenthesis) are in kcal/mol and with respect to the most stable ruthenium ethylidene complex **3.36** (an isomer of **3.12**, see Figure 4). For clarity, the chelating adamantyl group is not shown in the 3D transition state structures.

Reaction pathways initiated from both ruthenium methylidene and alkylidene complexes were investigated since these interconvert during the ethenolysis reaction. The most favorable pathway of the ethenolysis of *cis*-2-butene with catalyst **3.1** involves the side-bound approach of the internal olefin to the ruthenium methylidene complex **3.6** (Figure 2). Formation of the ruthenacyclobutane intermediate **3.8** requires an activation free energy of 8.8 kcal/mol (**TS3.7**). In **3.6**, **TS3.7**, and **3.8**, the nitrate is *syn* to the α-H on the chelating adamantyl group. Ruthenacyclobutane **3.8** isomerizes to form a less stable ruthenacycle **3.9**, in which the nitrate is

anti to the adamantyl α-H.[8] Cleavage of the ruthenacycle **3.9** via **TS3.10** requires a comparable activation energy as **TS3.7** ($\Delta G^{\ddagger}$ = 8.6 kcal/mol), and generates a ruthenium–propene π complex **3.11**. In contrast, productive cleavage of **3.8** without isomerization to **3.9** requires a much higher barrier ($\Delta G^{\ddagger}$ = 20.9 kcal/mol) and forms an unstable ruthenium ethylidene complex in which the ethylidene is *trans* to the chelating Ru–C bond. Thus, the isomerization to **3.9** is necessary before cleaving the ruthenacyclobutane. Decoordination of propene from **3.11** yields ruthenium ethylidene **12**, which then binds to an ethylene molecule to form π complex **3.13**. Subsequent steps involve the formation and cleavage of monosubstituted ruthenacyclobutane intermediates via **TS3.14** and **TS3.17**, respectively, and eventually regeneration of the ruthenium methylidene complex **3.6**. The monosubstituted transition states in the second half of the catalytic cycle (**TS3.14** and **TS3.17**) are both 3~4 kcal/mol more stable than the disubstituted transition states **TS3.7** and **TS3.10**. Thus, the reaction of ruthenium methylidene with the internal olefin is the rate-limiting step in the catalytic cycle (**TS3.7**), while the productive cleavage of the disubstituted metallacycle (**TS3.10**) requires essentially identical activation energy.

The anionic nitrate ligand binds bidentate to the ruthenium in all four transition states in the catalytic cycle, although the Ru–O bond *trans* to the alkylidene is significantly longer than the Ru–O bond *trans* to the NHC (~2.4 Å versus ~2.2 Å). The transition states with monodentate nitrate are five-coordinated with trigonal bipyramidal geometries and 1~4 kcal/mol less stable than the corresponding bidentate transition states (see experimental section). The small energy differences between mono- and bidentate nitrate complexes suggest that the monodentate transition structures might become favorable with bulkier olefin substituents and/or bulkier anionic ligands. Structures containing both mono- and bidentate binding modes are considered in the following computations and only the most favorable structures are shown.

In the analogous reaction with *trans*-2-butene, both transition states **TS3.18** and **TS3.21** are less stable than the corresponding transition states **TS3.7** and **TS3.10** in the reaction with *cis*-2-

butene (Figure 3). In **TS3.18** and **TS3.21**, one of the olefin substituents is pointing towards the *N*-mesityl group and leads to significant steric repulsions. The overall activation barrier is 5.2 kcal/mol higher than the ethenolysis of *cis*-2-butene. This explains the observed *Z*-selectivity in ethenolysis reactions.[9]

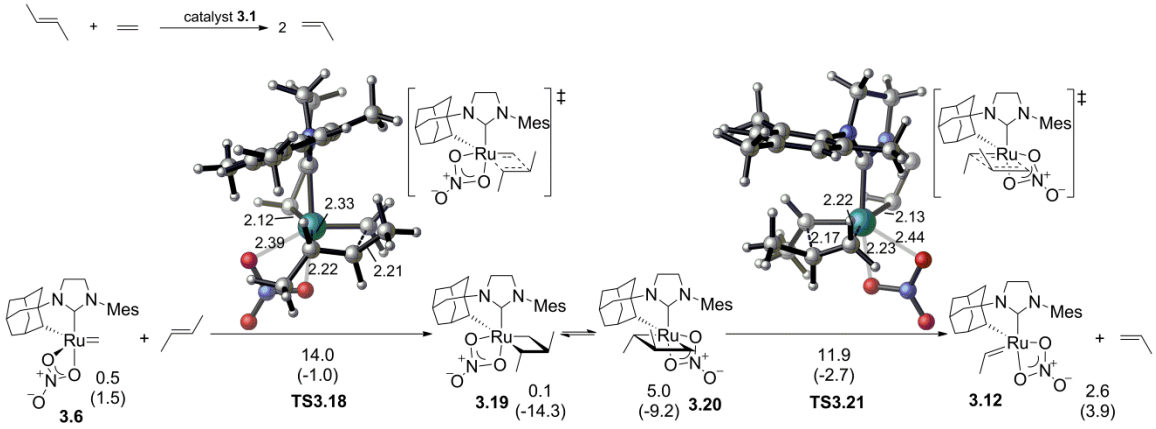


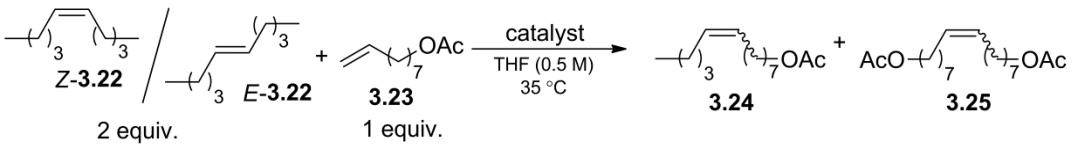
Figure 3: The most favorable pathway of ethenolysis of *trans*-2-butene with catalyst **3.1**. Gibbs free energies and enthalpies (in parenthesis) are in kcal/mol and with respect to the most stable ruthenium ethylidene complex **3.36** (an isomer of **3.12**, see Figure 4). For clarity, the chelating adamantyl group is not shown in the 3D transition state structures. In subsequent steps, **3.12** reacts with ethylene to regenerate **3.6**. This is identical to the second half of the catalytic cycle in the reaction with *cis*-2-butene (see Figure 2).

Crossover Experimental Studies

Preliminary cross metathesis investigations (see Chapter 2) led us to believe that ethenolysis plays a major role in productive metathesis reactions catalyzed by **3.1** (Chapter 2). The cross metathesis reaction between a *cis*-internal olefin and a terminal olefin was monitored over time and it was revealed that internal olefins must be broken down by ethenolysis before a hetero-cross product can be generated; it was proposed that the required methylidene complex was generated by homodimerization of the terminal olefin substrate. In addition to this, no crossover was

observed when two *cis*-internal olefins were reacted in the presence of catalyst **3.1**, and it was suggested that this was due to high steric demands associated with forming trisubstituted ruthenacycles using this particular catalyst.[10] Since cross metathesis between two internal olefins is a common occurrence for previous generations of metathesis catalysts including molybdenum-based *Z*-selective catalysts like **3.5**, we desired to further probe this unique reactivity of catalyst **3.1**. Previously, compound **3.24** was synthesized by reacting the two terminal olefins 1-hexene and 8-nonenyl acetate in the presence of catalyst **3.1** (0.5 mol %), and proceeded with high yield (67%) and *Z*-selectivity (91%). We next explored whether catalysts **3.1** and **3.3** were alternatively able to form substrate **3.24** from (1) an internal olefin and a terminal olefin, or (2) two internal olefins. Catalysts **3.1** and **3.3** were both investigated in order to elucidate differences in reactivity, activity, and selectivity between the complexes with different chelate sizes.

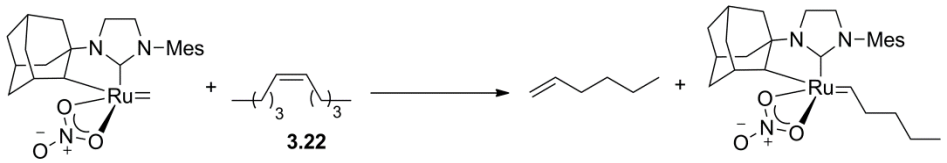
The reaction of the internal olefin 5-decene (**3.22**) and 8-nonenyl acetate (**3.23**) to form compound **3.24** was initially probed (Table 1). When catalyst **3.1** was employed, use of the *cis*- and *trans*- isomers of 5-decene greatly affected its metathesis activity (entries 1 and 2). Reaction with *cis*-5-decene led to formation of **3.24** with 57% yield and 91% *Z*-isomer at 0.2 mol % of **3.1**. The analogous reaction under the same conditions with *trans*-5-decene led to only trace amounts of **3.24**. In both cases, the undesired homodimer of 8-nonenyl acetate (compound **3.25**) was formed in similar quantities and *Z*-selectivities, regardless of the isomer of 5-decene used. Conversely, catalyst **3.3** was able to form compound **3.24** with both isomers of 5-decene (entries 3 and 4). The *Z*-selectivity of **3.24** and **3.25** were notably low compared to the reactions catalyzed by **3.1**, however this is attributed to extensive *Z*/*E* isomerization by secondary metathesis processes at the long reaction times.



entry	catalyst	mol %	substrate	time (h)	yield of 3.24[a]	yield of 3.25[a]	% *Z* of 3.24[b]	% *Z* of 3.25[b]
1	**3.1**	0.2	*Z*-**3.22**	6	57%	21%	91%	83%
2	**3.1**	0.2	*E*-**3.22**	24	<1%	19%	-	87%
3	**3.3**	2.5	*Z*-**3.22**	2	69%	14%	23%	22%
4	**3.3**	2.5	*E*-**3.22**	2	53%	17%	25%	33%

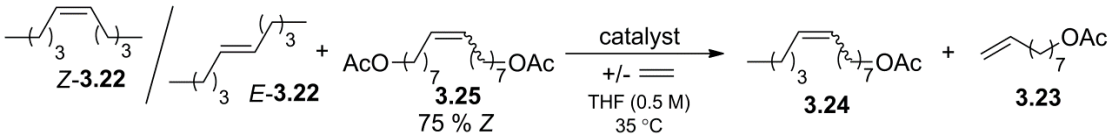
Table 1: Internal-terminal cross metathesis reaction of 5-decene (**3.22**) and 8-nonenyl acetate (**3.23**) catalyzed by **3.1** or **3.3**. [a] Determined by gas chromatography. [b] Determined by ^{1}H NMR.

The unique behavior of catalyst **3.1** gives important insight into the reactivity of this chelated catalyst.[11] Since **3.1** is effective for the *Z*-selective ethenolysis of internal olefins, its inability to react with *trans*-olefins in cross metathesis reactions further suggests that all internal olefins must undergo ethenolysis before they can react in a productive manner. In the reaction depicted in Table 1, it is proposed that a ruthenium methylidene is initially formed by homodimerization of 8-nonenyl acetate (**3.23**) that forms compound **3.25**. This methylidene can then react with *cis*-5-decene to form 1-hexene and the corresponding substituted alkylidene, both of which can react further with the terminal olefin 8-nonenyl acetate to generate cross product **3.24** (Scheme 1). Since 8-nonenyl acetate must initially be homodimerized for productive cross metathesis to occur, larger amounts of **3.25** will be generated compared to other catalysts, as was observed. It is also notable that because catalyst **3.3** is not particularly active as an ethenolysis catalyst, cross metathesis reactions catalyzed by **3.3** seems to proceed through different pathways that are more similar to previous generations of ruthenium catalysts, like **3.4**. In order to further test these hypotheses, the reactions of two internal olefins in the presence and absence of ethylene were carried out.



Scheme 1: Reaction of a methylidene with *cis*-5-decene to produce 1-hexene and the corresponding substituted alkylidene.

Exposure of catalyst **3.1** to a mixture of the internal olefins 5-decene (**3.22**) and **3.25** (75 % *Z*) under the conditions shown in Table 2 led to no formation of cross product **3.24** regardless of which isomer of 5-decene was employed (entries 1 and 2).[12,13] However, addition of 1 atm of ethylene into the headspace of the reaction vessel, followed by stirring for 4.5 hours led to formation of product **3.24** only when *cis*-5-decene was used (entry 3); no crossover was observed under these conditions with the *trans*-isomer (entry 4). This again supports the hypothesis that productive cross metathesis reactions involving internal olefins first proceed via *Z*-selective ethenolysis. In contrast, under the same conditions depicted in Table 2, catalyst **3.3** was able to catalyze the cross metathesis of two internal olefins in the absence of ethylene regardless of which isomer of 5-decene was employed (entries 5 and 6). Thus, cross metathesis reactions using catalyst **3.3** proceeds through a completely different pathway and, with this catalyst, trisubstituted ruthenacyclobutane intermediates are seemingly accessible. The low *E*/*Z* ratio is again attributed to extensive *Z*/*E* isomerization by secondary metathesis processes as evidenced by the degradation of **3.25** from 75% to 46% of the *Z*-isomer.



entry	catalyst	mol %	substrate	ethylene exposure[a]	time (h)	yield of	yield of 3.23[b]	% Z of	% Z of

						3.24[b]		3.24[c]	3.25[c]
1	**3.1**	1.0	*Z*-**22**	-	24	<1%	<1%	-	76%
2	**3.1**	1.0	*E*-**22**	-	24	<1%	<1%	-	75%
3	**3.1**	1.0	*Z*-**22**	+	4.5	21%	8%	95%	70%
4	**3.1**	1.0	*E*-**22**	+	24	<1%	2%	-	76%
5	**3.3**	2.5	*Z*-**22**	-	2	37%	<1%	31%	46%
6	**3.3**	2.5	*E*-**22**	-	2	30%	<1%	31%	60%

Table 2: Internal-internal cross metathesis reaction of 5-decene (**3.22**) with **3.25** catalyzed by **3.1** or **3.3**. [a] + = 1 atm of ethylene was introduced into the headspace of the reaction vessel. [b] Determined by gas chromatography. [c] Determined by ^{1}H NMR.

Crossover Computational Studies

We next employed computations to determine the activation energies to form and cleave the di- and trisubstituted ruthenacycle intermediates involved in reactions catalyzed by chelated catalysts **3.1** and **3.3**, and the non-chelated catalyst **3.4**. We first investigated the metathesis reactions of two internal *cis*-olefins with catalysts **3.1**, **3.3**, and **3.4**.[14] To simplify the calculations, we used trimethyl substituted ruthenacyclobutanes (i.e., the reaction of ruthenium ethylidene with *cis*-2-butenes) in the calculations as a model of the long conformationally mobile substrates used experimentally. Figure 4 shows the reactions of alkylidenes formed from catalysts **3.1**, **3.3**, and **3.4** with *cis*-2-butene. In these reactions, *trans*-2-butene is formed preferentially with catalyst **3.4**, and catalysts **3.1** and **3.3** give *cis*-2-butene product.

Reaction with the unchelated catalyst **3.4** (Figure 4a) forms *trans*-olefin product via the bottom-bound mechanism (i.e., the olefin approaches *trans* to the NHC ligand).[15,4] In the reactions with chelated catalysts **3.3** and **3.1**, the most favorable pathway involves the side-bound

mechanism (Figure 4b and 4c). The activation barrier of the reaction catalyzed by **3.1** is 5.6 and 3.7 kcal/mol higher than that with catalysts **3.4** and **3.3**, respectively ($\Delta G^{\ddagger}$ = 14.1 kcal/mol, **TS3.40**, compared to 8.5 and 10.4 kcal/mol, **TS3.29** and **TS3.34**). This suggests that formation of trisubstituted ruthenacyclobutanes with catalyst **3.1** is more difficult than with catalysts **3.4** and **3.3**, in agreement with the observed low crossover reactivities of **3.1** (Table 2).

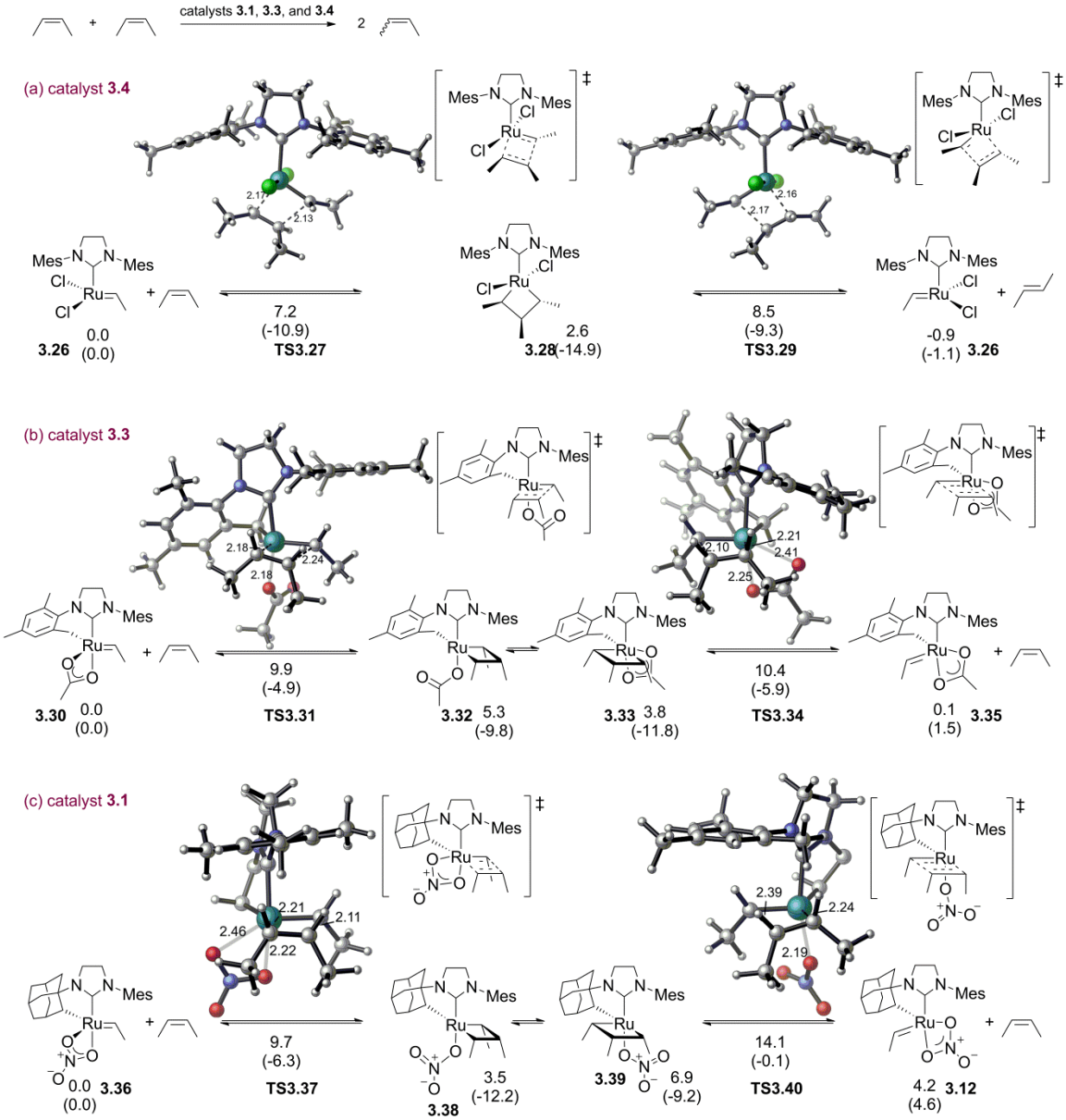


Figure 4: Reactions of ruthenium ethylidene complexes with *cis*-2-butene. These are the rate-determining steps in the metathesis of two *cis* internal olefins in the absence of ethylene. Free energies and enthalpies (in parenthesis) are given in kcal/mol with respect to the ruthenium alkylidene complexes (**3.26**, **3.30**, and **3.36**, respectively). For clarity, the chelating adamantyl group is not shown in the 3D structures of **TS3.37** and **TS3.40**.

The low crossover reactivity of catalyst **3.1** is attributed to one particular trisubstituted transition state, **TS3.40**, which is 4.4 kcal/mol less stable than the other trisubstituted transition state **TS3.37**. In **TS3.40**, the ethylidene is *syn* to the α-hydrogen on the chelating adamantyl group, while in **TS3.37** the ethylidene is *anti* to the α-hydrogen. Interestingly, **TS3.40** is the only transition state involving a nitrate ligand bound monodentate among all the transition states investigated in this study. Its bidentate isomer **TS3.40'** is 0.8 kcal/mol less stable, which is in contrast to other bidentate nitrate transition states that are typically 3 kcal/mol more stable than corresponding monodentate nitrate TS. To better illustrate the steric interactions with the nitrate ligand, "side-views" of the di- and trisubstituted transition states with catalyst **3.1** are shown in Figure 5. In the high energy trisubstituted transition state **TS3.40'**, the nitrate is located between the bulky chelating adamantyl group and one of the methyl substituents on the olefin. The distances between the nitrate and the olefin and between the nitrate and the adamantyl group are both significantly shorter than the sum of the van der Waals radii (the N–H distances are 2.57 and 2.51 Å, respectively, compared to the sum of van der Waals radii of N and H, 2.75 Å). The steric repulsions of the anionic nitrate ligand with the chelating adamantyl group and the substituent on the olefin clearly destabilize the bidentate transition state **TS3.40'** and force the hypothesized reaction to proceed via a generally less favorable monodentate transition state (**TS3.40**). As described earlier, the isomerization of the metallacyclobutane intermediate is necessary for a productive turnover. In the other trisubstituted metathesis transition state **TS3.37**, the nitrate is

located on the less crowded side that is *syn* to the α-adamantyl hydrogen. In **TS3.37**, the nitrate–adamantyl and nitrate–olefin distances are both longer than corresponding distances in **TS3.40'**. With the diminished steric repulsions with the nitrate, **TS3.37** is 5.4 kcal/mol more stable than **TS3.40'**. Thus, the rate-limiting step in the trisubstituted catalytic cycle is **TS3.40**.

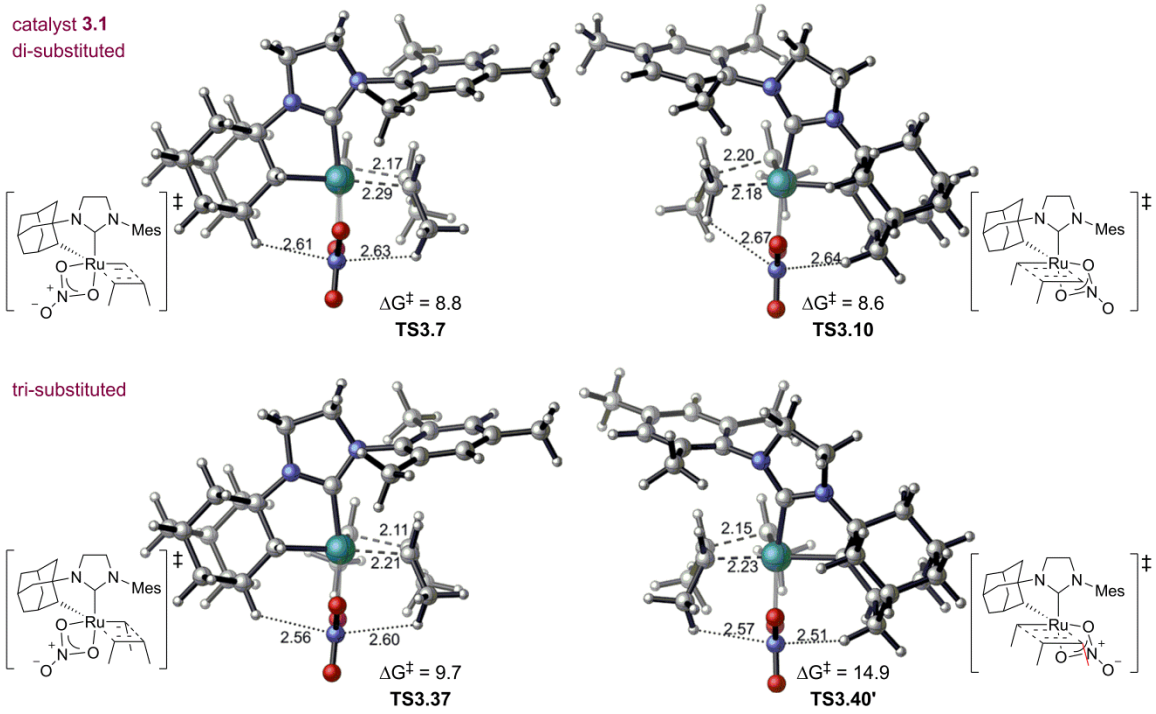


Figure 5: Side view of the dimethyl substituted transition states (**TS3.7** and **TS3.10**) and the trimethyl substituted **TS3.37** and **TS3.40'**. **TS3.40'** is destabilized due to steric repulsions of the nitrate with the chelating adamantyl group and the methyl group on the olefin.

In the presence of ethylene, ruthenium methylidene complexes are formed by the reaction of ethylene and ruthenium alkylidenes. The reaction of ruthenium methylidene **3.6** with *cis*-2-butene proceeds through disubstituted transition states **TS3.7** and **TS3.10** (Figure 2). **TS3.7** and **TS3.10** are both more stable than the corresponding trisubstituted transition states: **TS3.7** is only 0.9 kcal/mol more stable than **TS3.37** because of smaller steric repulsions of the internal olefin with

the methylidene rather than with the ethylidene (Figure 5). By replacing the methyl substituent with a hydrogen, **TS3.10** is dramatically stabilized by 6.3 kcal/mol compared to **TS3.40'**, due to alleviation of steric repulsions with the nitrate (see Figure 5 for direct comparison of the structures of di- and trisubstituted TS). The activation energy of the reaction of *cis*-2-butene with this methylidene is 5.3 kcal/mol lower than the corresponding pathway to form the trisubstituted ruthenacycle ($\Delta G^{\ddagger}$ = 8.8 kcal/mol, **TS3.7** compared to 14.1 kcal/mol, **TS3.10**). Thus, in the presence of ethylene, crossover products are formed, as was observed experimentally, from the reaction of internal olefins with the methylidene complex of catalyst **1** rather than with corresponding alkylidene complexes.

The trisubstituted metathesis pathways with catalysts **3.4** and **3.3** were also calculated and shown in Figure 4a and 4b. In contrast to the high activation barrier of the trisubstituted pathway with catalyst **3.1**, catalysts **3.4** and **3.3** both have lower activation barrier in the trisubstituted reaction ($\Delta G^{\ddagger}$ = 8.5 and 10.4 kcal/mol, respectively, compared to $\Delta G^{\ddagger}$ = 14.1 kcal/mol with **3.1**). This is attributed to less steric demand in the trisubstituted transition states with these catalysts; the chelating mesityl group in catalyst **3.3** is less bulky than the chelating adamantyl in **3.1**. With the unchelated catalyst **3.4**, the olefin approaches from the bottom, *trans* to the NHC ligand and thus there are no unfavorable ligand-substrate steric repulsions in the transition states.

As a comparison with the disubstituted pathway of catalyst **3.1** (Figure 2), we also computed the activation barriers of the reactions of *cis*-2-butene and the ruthenium methylidenes derived from catalysts **3.4** and **3.3** (Figure 6a and 6b, respectively). For the unchelated catalyst **3.4**, the reaction of *cis*-2-butene with methylidene **3.41** requires an activation energy of 8.9 kcal/mol. This is slightly higher than the barrier in the reaction with corresponding ethylidene **3.26** ($\Delta G^{\ddagger}$ = 8.5 kcal/mol, Figure 4a). This is attributed to fact that ruthenium methylidene **3.41** is 5.8 kcal/mol less stable than corresponding ethylidene **3.26** as well as the absence of unfavorable ligand-substrate steric repulsions in the trisubstituted transition states. The reaction of *cis*-2-butene with

the methylidene complex of catalyst **3.3** (**3.45**) requires a slightly lower activation energy than corresponding ethylidene (**3.30**) ($\Delta G^{\ddagger}$ = 8.7 kcal/mol compared to 10.4 kcal/mol). With both catalysts **3.4** and **3.3**, the differences between di- and trisubstituted activation barriers are within 1~2 kcal/mol. This suggests that the rate of crossover of internal olefins will not be significantly affected by the exposure to ethylene.

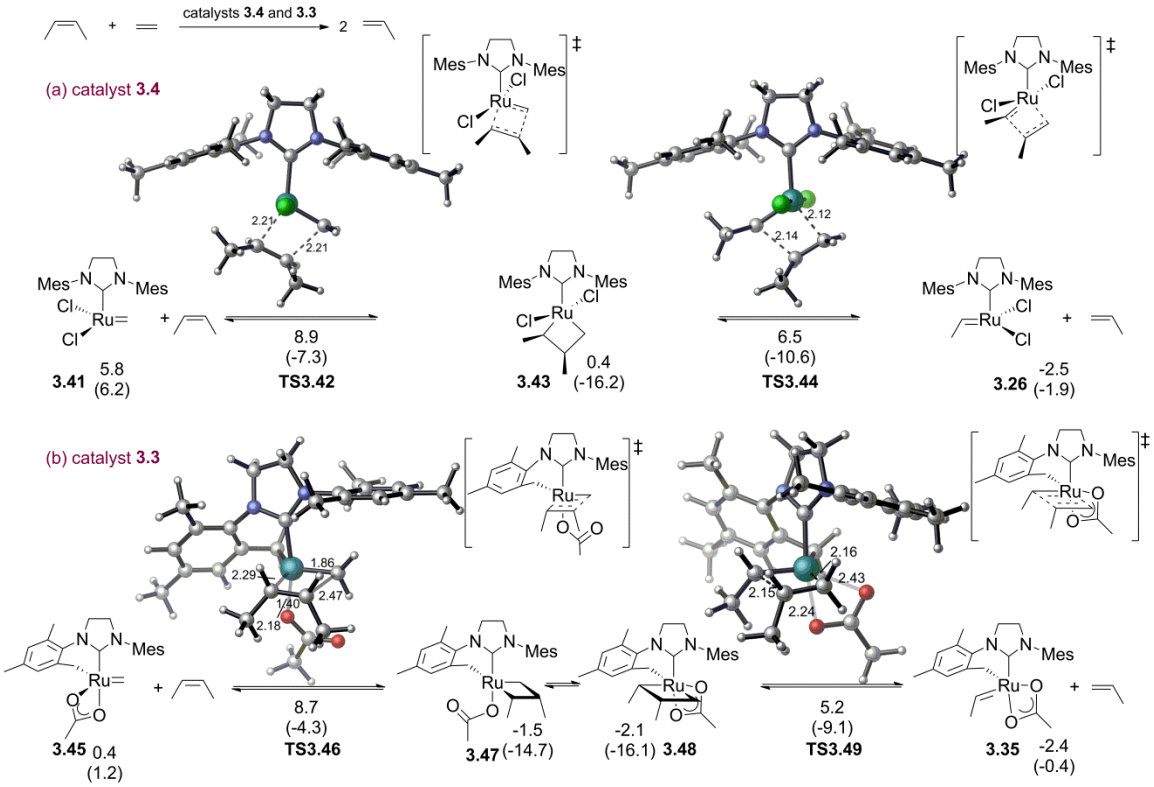


Figure 6: Free energies and enthalpies (in parenthesis) of the reaction of ruthenium methylidene complexes with *cis*-2-butene catalyzed by (a) catalyst **3.4** and (b) catalyst **3.3**. These are the rate-determining steps in the ethenolysis of internal olefins. All energies are with respect to the ruthenium ethylidene complexes (**3.26** and **3.30**, see Figure 4) and are given in kcal/mol. See Figure 2 for the reaction catalyzed by catalyst **3.1**.

To complete the computational investigations, another two scenarios involving disubstituted ruthenacyclobutanes, homodimerization and non-productive metathesis of terminal olefins, were also computed and the detailed results are provided. The homodimerization pathways of propene to form *E*- or *Z*-2-butene with catalysts **3.4**, **3.3**, and **3.1** are shown in Figure 7, and the competing non-productive reactions of propene and ruthenium ethylidenes are shown in Figure 8.[16] The computations predicted that the non-productive equilibration with catalysts **3.4** and **3.3** both requires lower activation barrier than the corresponding productive homodimerization pathway. In contrast, with catalyst **3.1**, the non-productive pathway requires 1.5 kcal/mol higher activation energy than homodimerization (12.7 kcal/mol compared to 11.2 kcal/mol). Similar to the trisubstituted transition state, the 1,3-disubstituted non-productive transition state is destabilized by steric repulsions with the nitrate, which is also located between the adamantyl and the methyl substituent on the olefin.

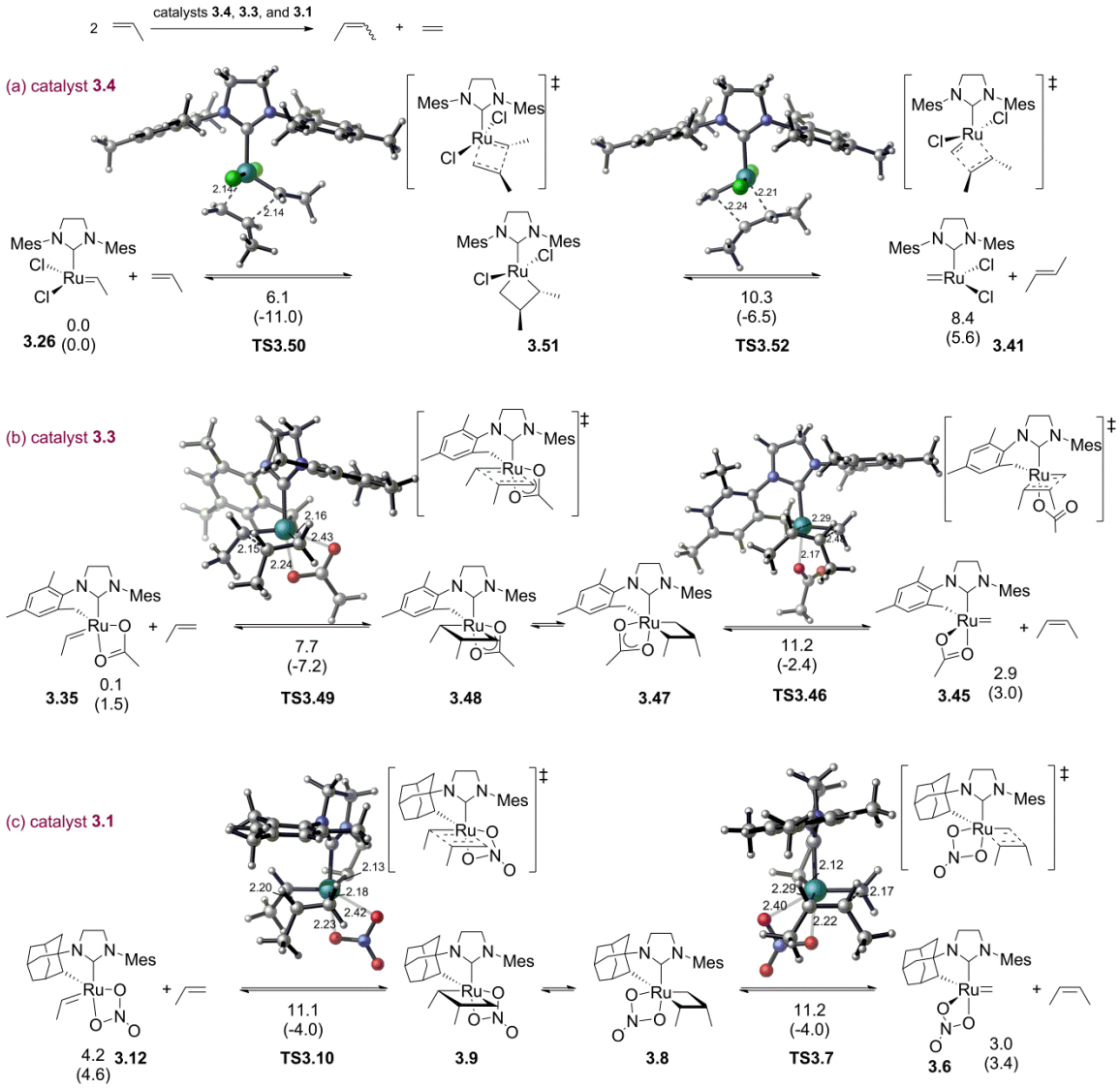


Figure 7: Free energies and enthalpies (in parenthesis) of the reaction of propene with ruthenium ethylidene complexes from (a) catalyst **3.4**; (b) catalyst **3.3**; and (c) catalyst **3.1**. All energies are with respect to the most stable isomer of ruthenium alkylidene complexes (**3.26**, **3.30**, and **3.36**, respectively) and are given in kcal/mol. For clarity, the chelating adamantyl group is not shown in the 3D structures of **TS3.7** and **TS3.10**.

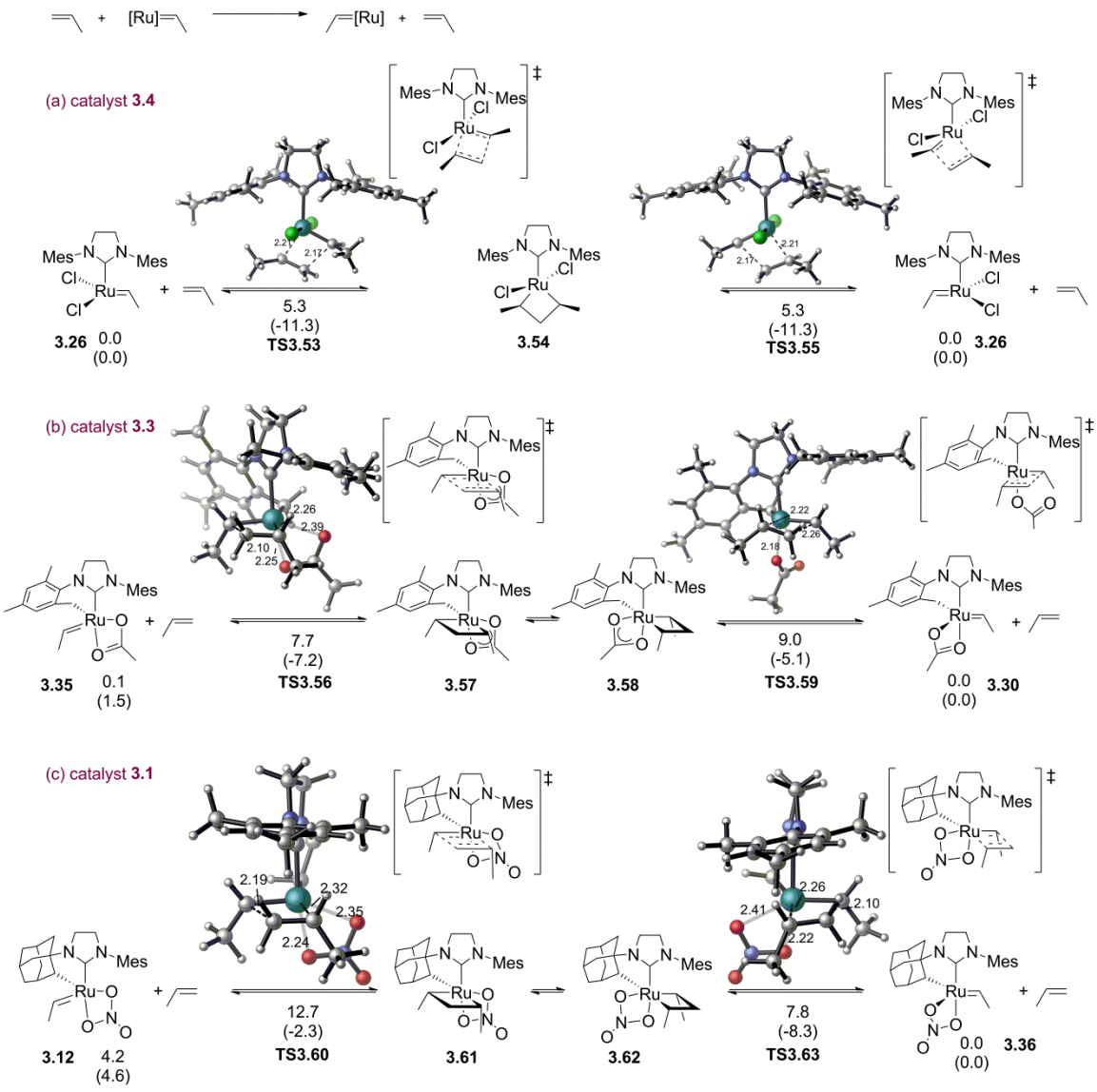


Figure 8: Free energies and enthalpies (in parenthesis) of the transition states and ruthenacyclobutane intermediates in the non-productive metathesis pathways of the reaction of propene and ruthenium ethylidene complexes from (a) catalyst **3.4**; (b) catalyst **3.3**; and (c) catalyst **3.1**. All energies are with respect to the most stable isomer of ruthenium alkylidene complexes (**3.26**, **3.30**, and **3.36**, respectively) and are given in kcal/mol. For clarity, the chelating adamantyl group is not shown in the 3D structures of **TS3.60** and **TS3.63**.

In summary, we have investigated the ethenolysis behavior of a new class of ruthenium metathesis catalysts, **3.1** and **3.3**, containing chelating NHC ligands. **3.1** was capable of catalyzing *Z*-selective ethenolysis reactions at low ethylene pressures (1-5 atm). DFT calculations revealed that the *Z*-selectivity in ethenolysis reactions catalyzed by **3.1** is a result of steric effects that prohibit *E*-olefins from productively reacting with the corresponding methylidene. Two internal olefins were unable to undergo cross metathesis in the presence of **3.1** to form cross products, but must first react with ethylene, or a synthetic equivalent, to form the corresponding terminal olefins. In addition to this, no crossover was observed when *trans*-internal olefins were employed as substrates in cross metathesis reactions. This implies that the *Z*-selective ethenolysis behavior of **3.1** plays a large role not only in its ethenolysis reactivity, but also in its cross metathesis reactivity. In contrast, six-membered chelated catalyst **3.3** exhibited poor ethenolysis reactivity and was capable of catalyzing the crossover of two internal olefins in the absence of ethylene, and thus reacts by a different pathway compared to **3.1**. Density functional theory calculations revealed the origins of the different reactivities of catalysts **3.3** and **3.1** in the crossover of internal olefins. The low crossover reactivity of two internal olefins with catalyst **3.1** is attributed to the steric repulsions of the nitrate anionic ligand with the chelating adamantyl group and the olefin substituent in the trisubstituted metathesis transition state. In ethenolysis reactions with catalyst **3.1**, similar steric control also prevents the ruthenium alkylidene from reacting with internal olefins. In contrast, the most favorable ethenolysis pathway catalyzed by **3.1** involves the reaction of an internal olefin with a ruthenium methylidene to avoid trisubstituted metathesis transition states. Catalyst **3.3** has a smaller mesityl chelating group, and thus the steric repulsions with the anionic ligand are diminished, making it capable to productively form and cleave trisubstituted metallacycles. In addition to providing important insight into the ethenolysis behavior of catalyst **3.1**, a better understanding of its cross metathesis reactivity has been gained and should provide important information for researchers planning on using this catalyst for a variety of applications.

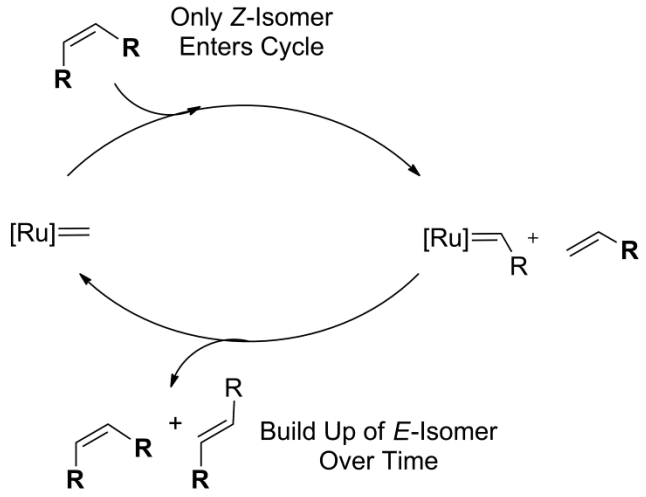
Z-DEGRADATION STUDIES:

In metathesis reactions catalyzed by adamantyl-chelated catalysts **3.1** and **3.2** (Figure 1),[17] the *Z*-olefin content degrades at higher reaction conversions and long reaction times. The rates of degradation are dependent on the identity of the catalyst, the substrate, and the reaction conditions. Because near perfect *Z*-selectivity is desired at high reaction conversions and long reaction times, an understanding of the mechanism of *Z*-degradation is highly necessary. This knowledge would enable us to showcase the numerous advantages of olefin metathesis in constructing *Z*-olefins compared to other common methods such as the Wittig reaction and poisoned hydrogenation. In the investigations described herein, *Z*-content degradation was monitored at reasonably long reaction times and at the temperatures and concentrations employed for previously reported metathesis reactions.

Z-Selective Ethenolysis Mechanism-

Since catalyst **3.1** has been shown to be effective as a *Z*-selective ethenolysis catalyst, it was proposed that this unique reactivity could be related to its propensity for *Z*-content degradation. This was suggested by the fact that carrying out terminal olefin homodimerization reactions in the presence of 1 atm of ethylene led to rapid and significant loss of *Z*-olefin content. It is envisioned that in metathesis reactions catalyzed by **3.1** using standard, previously reported conditions, a ruthenium methylidene will be formed that has near perfect selectivity for ethenolysis of *Z*-olefin isomers (Scheme 2). Reactions of the methylidene with a *Z*-internal olefin would form a terminal olefin and a substituted alkylidene. Subsequent reaction of these two species to form a methylidene and a new internal olefin will proceed with high, but not perfect *Z*-selectivity for the newly formed internal olefin. So if only *Z*-olefins undergo ethenolysis and a small amount of the *E*-isomer is formed every time two terminal olefins productively form an internal olefin, *Z*-olefins will slowly convert to *E*-olefins. If this cycle occurs many times, it could

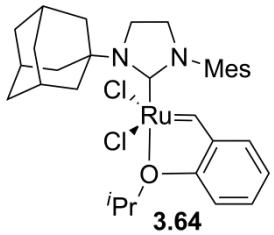
lead to the significant formation of *E*-olefins. Further investigations into this degradation mechanism are ongoing. It is envisioned that catalyst **3.2** will exhibit high *Z*-selective ethenolysis activity and selectivity, and thus this type of mechanism should apply to reactions catalyzed by **3.2** as well.



Scheme 2: *Z*-content degradation by *Z*-selective ethenolysis mechanism.

Metathesis Active Decomposition Product Mechanism-

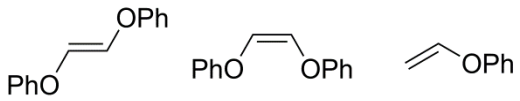
It was previously proposed that the observed *Z*-degradation could be caused by a metathesis active decomposition product derived from chelated catalysts **3.1** and **3.2**. No such species have been observed; however, complexes derived from cleavage of the chelating ruthenium-carbon bond were envisioned. Addition of the inorganic acid HCl to complex **3.3** causes cleavage of the chelating ruthenium-carbon bond, but maintains an intact alkylidene. As a result of this, we tested complex **3.64**, the unchelated analog of catalysts **3.1**, for its ability to cause *Z*-degradation of different internal olefins (Figure 9). Complex **3.64**, however, was completely inactive at both cross metathesis and *E*/*Z* isomerization reactions. The formation of unchelated complexes has never been observed during metathesis reactions and it is suggested that even if such species do form, they are not responsible for *Z*-content degradation.



3.64

Figure 9: Unchelated analog of complex **3.1**.

Another way to investigate this phenomenon was derived. It was assumed that any metathesis active decomposition products formed would react with compound *trans*-**3.65**, a diphenylether, to form a catalytically inactive Fischer carbene complex (Figure 10). Conversely, since it has been uniquely shown that chelated catalyst **3.1** is effective as a *Z*-selective ethenolysis catalyst, it is proposed that both the substituted alkylidene and methylidene analogs of catalyst **3.1** (and catalyst **3.2**) would not react with *trans*-**3.65** to an appreciable extent. If both of these propositions were true, and metathesis active decomposition products are formed and responsible for Z-degradation, addition of *trans*-**3.65** to a metathesis reaction catalyzed by **3.1** and **3.2** should theoretically hinder *Z* to *E* isomerization.



trans-**3.65** *cis*-**3.65** **3.66**

Figure 10: Vinyl ether additives.

Vinyl ether compounds *trans*-**3.65,** *cis*-**3.65**, and the terminal olefin analog, phenyl vinyl ether (**3.66**) were thus synthesized according to literature precedence.[18] The homodimerization reactions of allylbenzene and 4-penten-1-ol catalyzed by **3.1** and **3.2** were monitored over time with and without the addition of one of the vinyl ether additives. Addition of phenyl vinyl ether

(**3.66**) completely prevented productive conversion to the desired cross product with both catalysts **3.1** and **3.2**, as was expected. When *cis*-**3.65** was used as an additive, conversion to the cross product for both substrates and catalysts was significantly inhibited. The low conversions observed are rationalized by the need to generate ruthenium methylidenes before reaction with internal olefins can occur (*vide supra*). It thus makes sense that there would be some conversion to desired homodimer product before the catalyst would be deactivated by the vinyl ether. Conversely, when *trans*-**3.65** was used as an additive, minimal reaction inhibition was observed. These data imply that catalysts **3.1** and **3.2** are active and selective for the ethenolysis of internal vinyl ethers in addition to aliphatic olefins. Interestingly, there was a smaller difference between the control reactions and the *trans*-**3.65** additive reactions for catalyst **3.2** compared to **3.1**, implying that catalyst **3.2** is more selective at *Z*-selective ethenolysis compared to **3.1**.

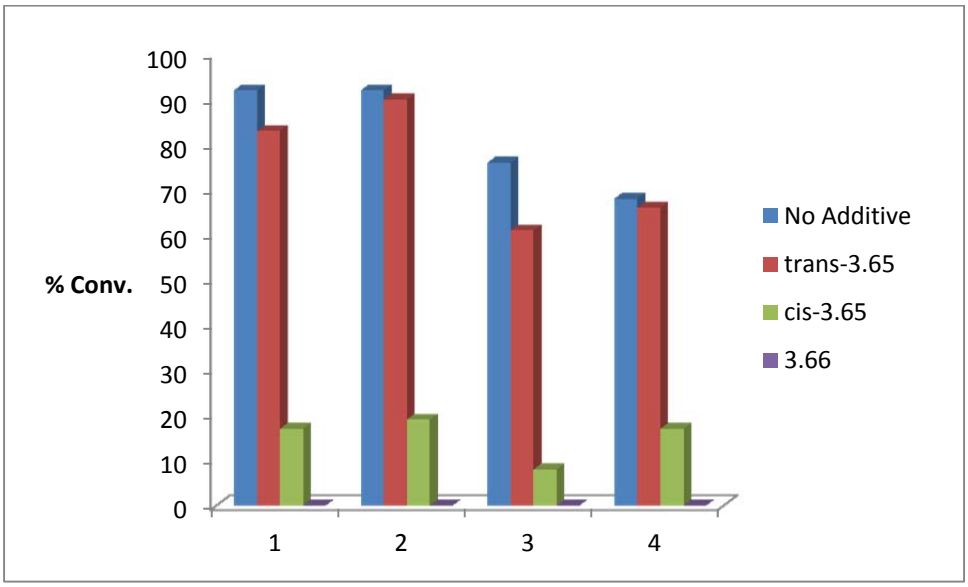


Figure 11: Homodimerization reactions with and without vinyl ether additives. 1 = allylbenzene homodimerization reaction catalyzed by catalyst **3.1**; 2 = allylbenzene homodimerization reaction catalyzed by catalyst **3.2**; 3 = 4-pentenol homodimerization reaction catalyzed by catalyst **3.1**; 4-pentenol homodimerization reaction catalyzed by catalyst **3.2**.

With this knowledge in hand, we wanted to test how addition of *trans*-**3.65** would influence the *E*/*Z* ratio of homodimerization reactions over time using different terminal olefin substrates. When *trans*-**3.65** was used as an additive in the homodimerization reaction of allylbenzene, an unexpected trend was observed. Instead of decreasing *Z*-degradation as was originally proposed, production of the *E*-isomer was accelerated (Figure 12). Conversely, no effect was seen when catalyst **3.2** was used in analogous reactions (Figure 13). Since catalyst **3.1** reacted with *trans*-**3.65** while catalyst **3.2** did not, it is proposed that the species responsible for this *Z*-degradation is a ruthenium Fischer carbene or a species derived from one. However, all attempts to isolate these types of species derived from catalysts **3.1** and **3.2** have been unsuccessful to this point. Fischer carbene complexes of ruthenium are generally considered inactive and vinyl ethers are used to quench metathesis reactions. Thus it is surprising that addition of a vinyl ether would affect the selectivity and activity of olefin metathesis reactions; further investigations into this phenomenon are ongoing.

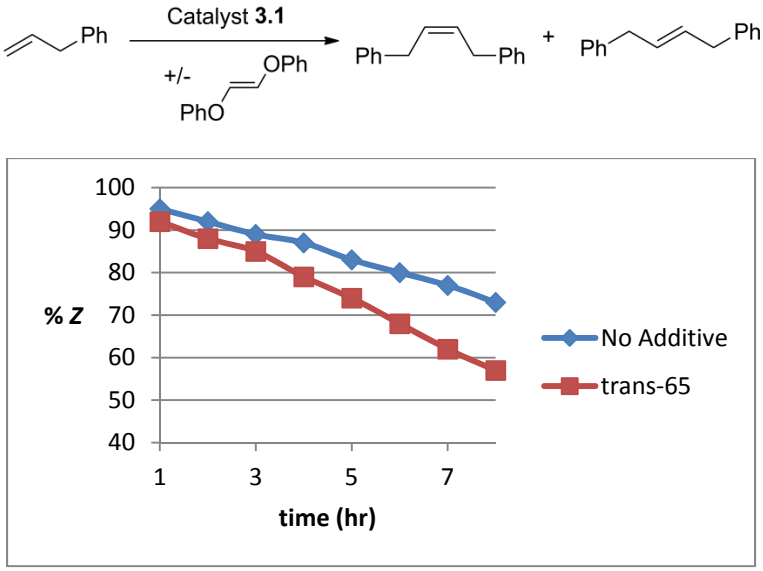


Figure 12: Addition of *trans*-**3.65** causes increased *Z*-degradation with catalyst **3.1** in allylbenzene homodimerization reactions.

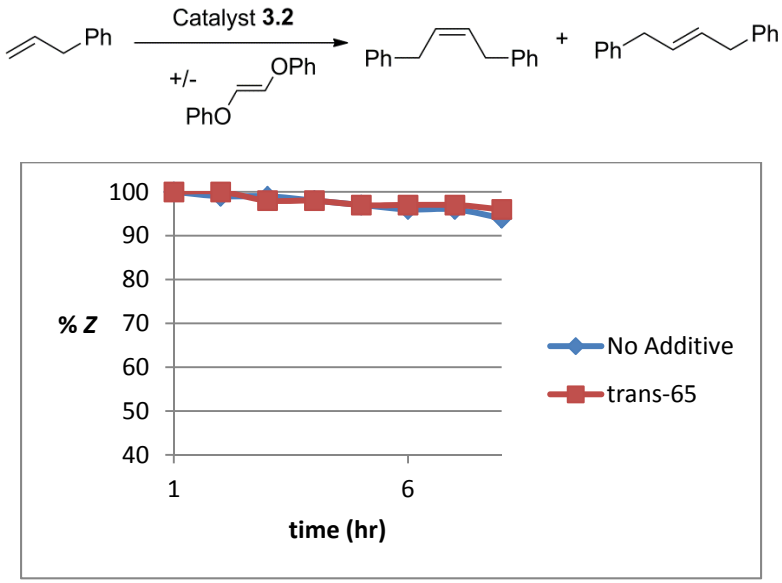


Figure 13: Addition of *trans*-**3.65** causes no noticeable change in *Z*-degradation with catalyst **3.2** in allylbenzene homodimerization reactions.

CONCLUSIONS:

During investigations into the cross metathesis reactivity of our family of catalysts containing a five-membered chelating architecture, it became evident that the metathesis mechanism was distinct from previous generations of catalysts. Experimental and theoretical investigations were thus carried out to elucidate the origins of observed trends in reactivity. For example, the cross metathesis of two internal olefins does not occur with this family of catalysts. Studies revealed that this effect was caused by a prohibitively high activation barrier for the formation and cycloreversion of trisubstituted metallacyclobutane intermediates. Thus, cross metathesis reactions that employ internal olefins must proceed via an initial ethenolysis event through a 1,2-disubtituted metallacyclobutane intermediate. Because of the *Z*-selective ethenolysis reactivity observed for catalysts **3.1** and **3.2**, only *Z*-internal olefins should be capable of undergoing productive metathesis reactions. Indeed, *E*-olefins were found to be unreactive

when used in cross metathesis reactions, even in the presence of ethylene. Six-membered chelated catalyst **3.3**, in contrast, was capable of catalyzing the cross metathesis of two internal olefins and reactions with *E*-internal olefins, a phenomenon that was explained using calculations. More recent efforts have been aimed at investigating if the *Z*-selective ethenolysis reactivity of five-membered chelated catalysts could have implications for *Z*-content degradation observed at long reaction times. Preliminary results have shown that addition of ethylene to metathesis reactions causes significant degradation of the *Z*-isomer.

References and Notes:

1. Marinescu, S. C.; Levine, D. S.; Zhao, Y.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2011**, *133*, 11512.

2. The catalyst loading used for the *E*-5-decene substrate was five times higher than for *Z*-5-decene.

3. It is envisioned that this *Z*-selective ethenolysis method can be used to purify products from reactions other than metathesis that produce *E*-olefins but that are not perfectly selective for their formation.

4. Gaussian 09, Revision B.01: Frisch, M. J *et al.* Gaussian, Inc., Wallingford CT, **2010**.

5. a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

6. a) Zhao,Y.; Truhlar, D. G. *Theor. Chem. Acc.*, **2008**, *120*, 215. b) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.*, **2008**, *41*, 157.

7. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G., *J. Phys. Chem. B* **2009,** *113*, 6378.

8. Isomerization of **3.8** to **3.9** occurs via monodentate nitrate complexes. See Experimental section for details.

9. However, theoretical calculations predicted much higher *Z*-selectivity than the observed relative rates of *E* and *Z* olefins.

10. It should be noted that analogous pivalate-substituted catalysts were also not able to catalyze the cross metathesis of two internal olefins and, as such, we believe that trisubstituted metallacycle intermediates are also unfavorable.

11. For analogous pivalate-substituted catalysts, it is thought that formation of a methylidene is possible and that the reaction proceeds via the same mechanism as with **3.5**, but reaction with a large excess of ethylene leads to decomposition.

12. Raising the temperature from 35 °C to 80 °C did not affect reactivity as formation of **3.24** was still not observed.

13. This suggests that the self-metathesis processes are prevented, helping explain the high selectivity observed in the ethenolysis of methyl oleate by catalyst **3.1**.

14. In order to simplify calculations, an acetate-substituted complex was used for modeling.

15. The competing pathway to form *cis*-2-butene requires a barrier of 8.7 kcal/mol, only 0.2 kcal/mol higher than the *trans* pathway, indicating poor *Z*/*E*-selectivity from kinetic control.

16. Computational studies of olefin homodimerization with catalysts **3.1** and **3.3** have already been reported: Liu, P.; Xu, X.; Dong, X.; Keitz, B. K.; Herbert, M. B.; Grubbs, R. H.; Houk, K. N. *Z*-Selectivity in Olefin Metathesis with Chelated Ru Catalysts: Computational Studies of Mechanism and Selectivity. *J. Am. Chem. Soc*. **2012**, *134*, 1464. Here we repeated some of the computations to make direct comparisons between different catalysts and between productive and non-productive metathesis.

17. Rosebrugh, L. E.; Herbert, M. B.; Marx, V. M.; Keitz, B. K.; Grubbs, R. H. *J. Am. Chem. Soc*. **2013**, *135*, 1276.

18. Yang, J.; Bauld, N. L. *J. Org. Chem*. **1999**, *64*, 9251.

Experimental Section:

General Information

All reactions were carried out in dry glassware under an argon atmosphere using standard Schlenk technique, or in a Vacuum Atmospheres Glovebox under a nitrogen atmosphere unless otherwise specified. Commercially available reagents were used as received unless otherwise noted. Substrates for ethenolysis and olefin cross metathesis were degassed with argon prior to use. Proton peaks in the ^{1}H NMR spectra corresponding to the *E*- and *Z*-isomers of all ethenolysis substrates were confirmed by HSQC analysis. THF was purified by passage through solvent purification columns and further degassed with bubbling argon. C_6D_6 was purified by passage through a solvent purification column. $CDCl_3$ and acetone-d_6 were used as received.

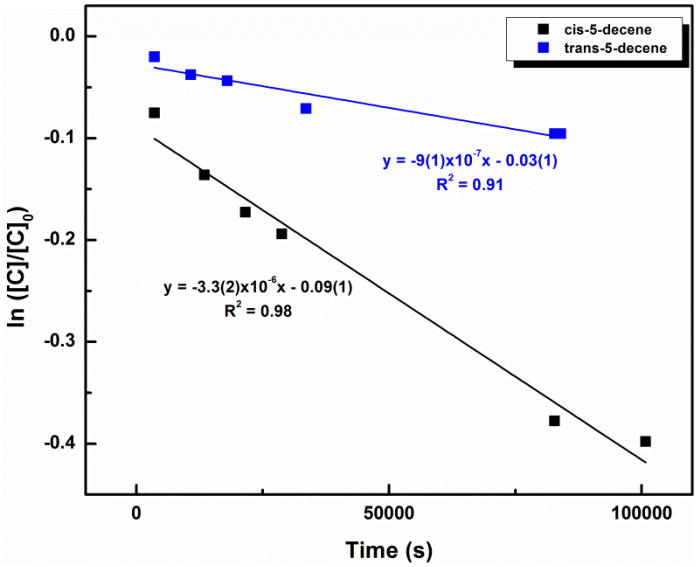
^{1}H and ^{13}C NMR spectra were recorded on a Varian 500 MHz spectrometer. Chemical shifts are reported in ppm downfield from Me_4Si by using the residual solvent peak as an internal standard. Spectra were analyzed and processed using MestReNova Ver. 7.1. High-resolution mass spectra were provided by the California Institute of Technology Mass Spectrometry Facility using JEOL JMS-600H High Resolution Mass Spectrometer. Gas chromatography data were

obtained using Agilent 6850 FID gas chromatograph equipped with HP-5 (5%-phenyl)-methylpolysiloxane capillary column (Agilent).

Kinetic measurement procedure:

In a glovebox, **3.1** (23 mg, 0.036 mmol) and anthracene (internal standard, 69 mg, 0.49 mmol) were dissolved in 5 mL of C_6D_6 (ca. 0.0072 M in catalyst). A portion (13 µL) of this solution was added to a J. Young NMR tube followed by C_6D_6 (570 µL) and olefin (10 µL, 0.095 mmol). The tube was quickly sealed, removed from the glovebox, cooled to -78 °C and freeze-pump-thawed (x3). After the final freeze-pump-thaw cycle, the NMR tube was backfilled with an atmosphere of ethylene, sealed, and allowed to warm to RT. An initial NMR spectrum was taken at RT to get initial concentrations after which the tube was placed in a 50 °C oil bath. Over a period of ca. 24 h, the NMR tube was periodically removed from the oil bath and the reaction was analyzed by NMR spectrometry.

The ethenolysis of *cis*-5-decene reached a maximum of 30% while that of *trans*-5-decene was 10%. Therefore, the first-order kinetic plots below only take into account the early stages of the reaction, before equilibrium is established.



Alternatively, at these low concentrations, the method of initial rates can be used to compute the ratio of d[*cis*-5-decene]/dt to d[*trans*-5-decene]/dt. As shown in the table below, the ratio of the rates derived from the method of initial rates is similar to the ratio of the rate constants obtained from the linear fits in the figure above.

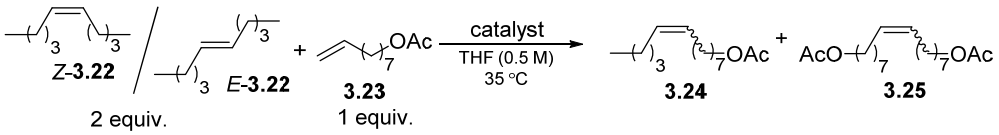
d[*cis*-5-decene]/dt	**d[*trans*-5-decene]/dt**	**ratio**
1.5×10^{-6}	4.3×10^{-7} M s^{-1}	3.4

GC Data Analysis for Cross Metathesis

To obtain accurate conversion data, GC response factors for all starting materials and products (ethylene and 1-hexene excluded) were obtained and GC data was analyzed. Tridecane was used as an internal standard. Samples for GC analysis were obtained by adding ca. 10-30 μL of the reaction mixture to 1 ml of ethyl vinyl ether. The resulting sample was shaken, allowed to stand for 5 min, and then analyzed via GC.

GC instrument conditions: inlet temperature: 250 °C; detector temperature: 250 °C; hydrogen flow: 30 ml/min; air flow: 400 ml/min.; constant col + makeup flow: 25 ml/min.

GC Method: A) 50 °C for 4 min, followed by a temperature increase of 6 °C/min to 300 °C and a subsequent isothermal period at 300 °C for 5 min. or B) 50 °C for 2 min, followed by a temperature increase of 12 °C/min to 110 °C and a subsequent isothermal period at 110 °C for 2 min. ~ a temperature increase of 6 °C/min to 115 °C and a subsequent isothermal period at 115 °C for 0.5 min. ~ a temperature increase of 5 °C/min to 140 °C. ~ a temperature increase of 12 °C/min to 210 °C and a subsequent isothermal period at 210 °C for 2 min. ~ a temperature increase of 6 °C/min to 250 °C ~ a temperature increase of 15 °C/min to 300 °C and a subsequent isothermal period at 300 °C for 5 min.

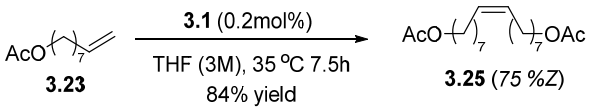


Representative procedure for cross metathesis of 3.23 with *cis*-5-decene (*Z*-3.22) or *trans*-5-decene (*E*-3.22) with catalyst 3.1:

In a glovebox, a 5 ml vial with a magnetic stir bar was charged with *cis*-5-decene (370 μL, 280 mg, 2.0 mmol) or *trans*-5-decene (370 μL, 280 mg, 2.0 mmol), 8-noneyl acetate (**3.23**) (210 μL, 180 mg, 1.0 mmol) and tridecane (120 μL, 92 mg, 0.50 mmol). A solution of catalyst **3.1** was prepared in THF. THF and the desired volume of the catalyst solution were added to the reaction mixture [THF total 1.3 mL and **3.1** (1.3 mg, 0.0020 mmol)]. (Before adding the catalyst, an aliquot was taken for GC analysis to check the molar ratio of each compound at the starting point.) The vial was sealed with a screw-cap and then stirred at 35 °C. After the reaction solution was allowed to stir for 6 h, an aliquot was taken for GC analysis to obtain the yield. The vessel was removed from the glovebox and left open to air, and then the reaction solution was transferred to a 50 ml flask with using ethyl vinyl ether (ca. 10 ml). After stirring overnight at room temperature, the mixture was concentrated *in vacuo*. The resulting mixture was separable by flash column chromatography (SiO_2; *n*-hexane ~ ethyl acetate/*n*-hexane=1/40 ~ 1/30 ~ 1/9) to give pure **3.24**, **3.23**, and **3.25** as colorless oils. The NMR data for **3.24** matched literature precedence.

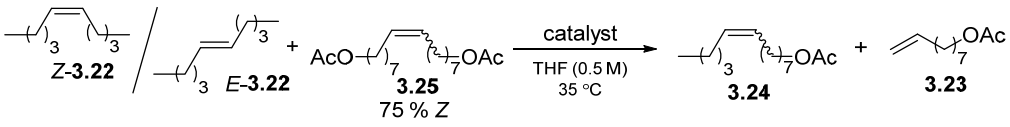
Procedure for cross metathesis of 3.23 with *cis*-5-decene (*Z*-3.22) or *trans*-5-decene (*E*-3.22) with catalyst 3.3: According to the above procedure, *cis*-5-decene (190 μl, 140 mg, 1.0 mmol) or *trans*-5-decene (190 μl, 140 mg, 1.0 mmol), 8-noneyl acetate (**3.23**) (105 μl, 90 mg, 0.5 mmol)

and tridecane (60 µl, 46 mg, 0.25 mmol) were added to a 5 mL vial. A solution of catalyst **3.3** was prepared in THF. THF and the desired volume of the catalyst solution were added to the reaction mixture [THF total 0.65 mL and **3.3** (8.2 mg, 0.013 mmol)]. These reactions were worked up according to the above procedure.



Synthesis of *Z*-3.25

In a glovebox, a 20 ml vial was charged with 8-nonenyl acetate (**3.23**) (3.2 g, 17 mmol) and **3.1** (22 mg, 0.035 mmol) and THF (6.0 ml). The vial was sealed with a screw-cap and then stirred at 35 °C for 7.5 h. The vessel was removed from the glovebox and left open to air, and then the reaction solution was transferred to a 50 ml flask with using ethyl vinyl ether (ca. 10 ml). After stirring for overnight at room temperature, the mixture was concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (SiO_2; ethyl acetate/*n*-hexane=1/50 ~ 1/20 ~ 1/4) to give pure **3.25** (2.5 g, 7.3 mmol, 84% yield, 75 %*Z*) as a colorless oil. The NMR data for **3.25** matched that reported earlier in the supporting information.

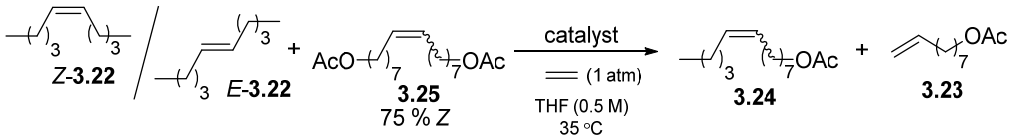


Representative procedure for cross metathesis of *cis*-5-decene (*Z*-3.22) or *trans*-5-decene (*E*-3.22) with 3.25 *without ethylene* in the presence of catalyst 3.1:

In a glovebox, a 5 ml vial with a magnetic stir bar was charged with *cis*-5-decene (95 µl, 70 mg, 0.5 mmol) or *trans*-5-decene (95 µl, 70 mg, 0.5 mmol), **3.25** (170 mg, 0.50 mmol, 75 %Z) and tridecane (61 µl, 46 mg, 0.25 mmol). A solution of catalyst **3.1** was prepared in THF. THF and the desired volume of the catalyst solution were added to reaction mixture [THF total 675 µl and **3.1** (3.2 mg, 0.0050 mmol)]. (Before adding the catalyst, an aliquot was taken for GC analysis to check the molar ratio of each compound at the starting point.) The vial was sealed with a screw-cap and then stirred at 35 °C. After the reaction solution was allowed to stir for 2 h, an aliquot was taken for GC analysis to obtain the yield. The vessel was removed from the glovebox and left open to air, and then the reaction solution was transferred to a 50 ml flask with using ethyl vinyl ether (ca. 10 ml). After stirring for overnight at room temperature, the mixture was concentrated *in vacuo*. The resulting mixture was separable by flash column chromatography (SiO_2; *n*-hexane ~ ethyl acetate/*n*-hexane=1/40 ~ 1/30 ~ 1/9) to give pure **3.24**, **3.23**, and **3.25** as colorless oils.

Procedure for cross metathesis of *cis*-5-decene (*Z*-3.22) or *trans*-5-decene (*E*-3.22) with 3.25 *without ethylene* in the presence of catalyst 3.3:

In a glovebox, a 5 ml vial with a magnetic stir bar was charged with *cis*-5-decene (95 µl, 70 mg, 0.5 mmol) or *trans*-5-decene (95 µl, 70 mg, 0.5 mmol), **3.25** (170 mg, 0.50 mmol, 75 %Z) and tridecane (61 µl, 46 mg, 0.25 mmol). A solution of catalyst **3.3** was prepared in THF. THF and the desired volume of the catalyst solution were added to reaction mixture [THF total 675 µl and **3.3** (8.2 mg, 0.013 mmol)]. These reactions were worked up according to the above procedure.



Representative procedure for cross metathesis of *cis*-5-decene (*Z*-3.22) or *trans*-5-decene (*E*-3.22) with 3.25 *with ethylene* in the presence of catalyst 3.1:

In a glovebox, a 5 ml vial with a magnetic stir bar was charged with *cis*-5-decene (94 μl, 70 mg, 0.50 mmol) or *trans*-5-decene (94 μl, 70 mg, 0.50 mmol), **3.25** (170 mg, 0.50 mmol, 75 %Z) and tridecane (61 μl, 46 mg, 0.25 mmol). A solution of catalyst **3.1** was prepared in THF. THF and the desired volume of the catalyst solution were added to reaction mixture [THF total 675 μl and **3.1** ((3.2 mg, 0.0050 mmol))]. (Before adding the catalyst, an aliquot was taken for GC analysis to check the molar ratio of each compound at the starting point.) The reaction solution was sealed with a screw-cap septum top, removed from the glovebox, equipped with an ethylene balloon, and then purged with ethylene before heating. After the reaction solution equipped with the ethylene balloon was allowed to stir at 35 °C for 2 h, the vial was brought in the glovebox again. The reaction mixture was stirred at 35 °C while open to the glovebox atmosphere. After the reaction solution was allowed to stir for 4.5 h, an aliquot was taken for GC analysis to obtain the yield. The vessel was removed from the glovebox and left open to air, and then the reaction solution was transferred to a 50 ml flask with using ethyl vinyl ether (ca. 10 ml). After stirring for overnight at room temperature, the mixture was concentrated *in vacuo*. The resulting mixture was separable by flash column chromatography (SiO_2; *n*-hexane ~ ethyl acetate/*n*-hexane=1/40 ~ 1/30 ~ 1/9) to give pure **3.24**, **3.23**, and **3.25** as colorless oils.

Computational Details

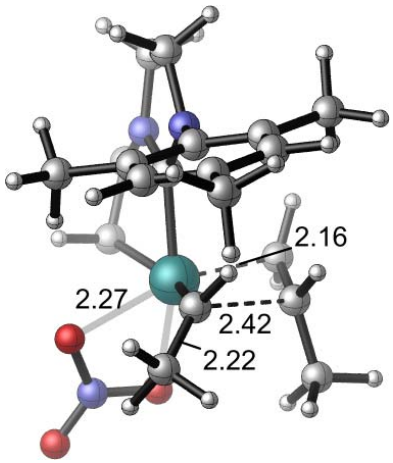
The geometries of all intermediates and transition states were optimized with B3LYP in gas phase. A mixed basis set of LANL2DZ for Ru and 6-31G(d) for other atoms were used in geometry optimizations. Single point energy calculations were performed with the M06 functional and a mixed basis set of SDD for Ru and 6-311+G(d,p) for other atoms. The SMD solvation model was used in M06 single point energy calculations. THF was used as solvent. The

reported free energies and enthalpies include zero-point energies and thermal corrections calculated at 298K by B3LYP. All calculations were performed with Gaussian 09. The 3D structures of molecules were generated using CYLView (http://www.cylview.org).

The Gibbs free energies in Gaussian were calculated under p = 1 atm. The standard free energies in solution were calculated under the standard state in solution, i.e., M = 1 mol/L. The correction was made by adding $RT \ln(c_{0s}/c_{0g})$ (i.e., about 1.84 kcal/mol) to energies of all structures, where c_{0s} is the standard molar concentration in aqueous solution (1 mol/L), c_{0g} the standard molar concentration in gas phase (0.0446 mol/L), and R the gas constant.

Direct productive cleavage of ruthenacyclobutane 3.8

In the ethenolysis of *Z*-2-butene with catalyst **3.1** (Figure 2), the first metathesis transition state **TS3.7** leads to a ruthenacyclobutane intermediate **3.8**, in which the nitrate is syn to the α-H atom on the chelating adamantyl group. Direct productive cleavage of **3.8** via metathesis transition state **TS3.10'** would lead to a propene-ruthenium ethylidene complex, an isomer of **3.11**. This direct cleavage pathway is highly unfavorable due to the high activation energy of **TS3.10'** ($\Delta G^{\ddagger}$ = 20.9 kcal/mol). Thus, **3.8** undergoes isomerization (see next page for more details) to form another ruthenacyclobutane intermediate **3.9**, in which the nitrate is anti to the α-H atom on the adamantyl. Subsequent productive cleavage of **3.9** is much more favorable than the direct cleavage of **3.8** via **TS3.10'**. The 3D structure of **TS3.10'** is shown below. In **TS3.10'**, the forming alkylidene is *trans* to the chelating adamantyl group. Both alkylidene and adamantyl are strongly electron-donating ligands and thus prefer to not be *trans* to each other due to trans influences.

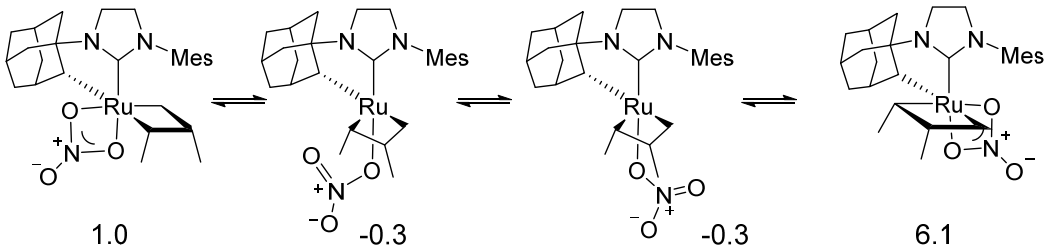


TS3.10'

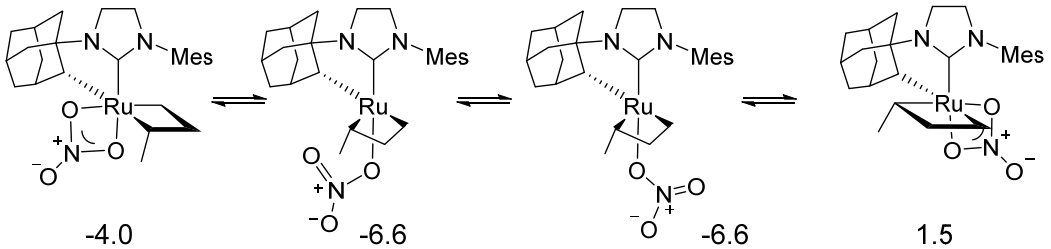
$\Delta G^{\ddagger}$ = 20.9 kcal/mol

Interconversion of Ruthenacyclopropane Intermediates 3.8 and 3.9

The interconversion of the ruthenacyclopropane intermediates **3.8** and **3.9** occurs via monodentate nitrato complexes **3. 8'** and **3.9'**, which are five-coordinated trigonal bipyramidal geometry. Both **3.8'** and **3.9'** are lower in energy than corresponding bidentate nitrato complexes. The interconversion between **3.8'** and **3.9'** involves rotation of the Ru–O dative single bond. This rotation step is expected to have low barrier. Thus, the interconversion between **3.8** and **3.9** should be facile.

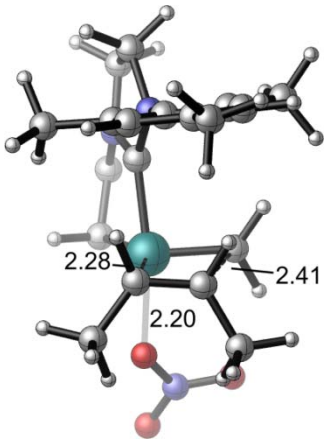


Similarly, the interconversion between the mono-substituted ruthenacyclobutane intermediates **3.16** and **3.15** also readily occurs via stable monodentate intermediates **3.16'** and **3.15'**.

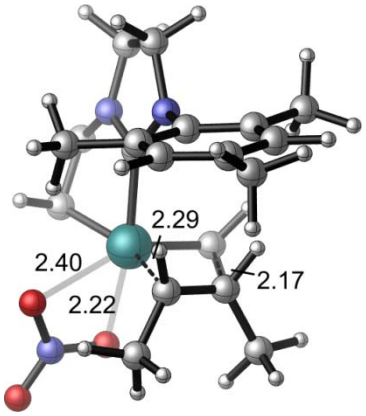

Mes
Ru
-4.0
(-16.6) **3.16**
-6.6
(-19.0) **3.16'**
3.15' (-19.2)
1.5
(-11.7)**3.15**

Monodentate Transition State Structures

In the ethenolysis reaction of *Z*-2-butene with catalyst **3.1**, the nitrate binds to the ruthenium in a bidentate fashion in all four metathesis transition states in the catalytic cycle (Figure 2). The monodentate TS structures are 1~4 kcal/mol less stable than corresponding bidentate TSs. The 3D structures of the rate-determining transition state **TS3.7** and the monodentate nitrato isomer (**TS3.72-mono**) are shown below. The chelating adamantyl groups are not shown for clarity.



TS3.7-mono
$\Delta G^{\ddagger}$ = 9.4 kcal/mol
$\Delta H^{\ddagger}$ = -2.9 kcal/mol



TS3.7
$\Delta G^{\ddagger}$ = 8.8 kcal/mol
$\Delta H^{\ddagger}$ = -5.8 kcal/mol

Appendix A

CRYSTALOGRAPHIC DATA

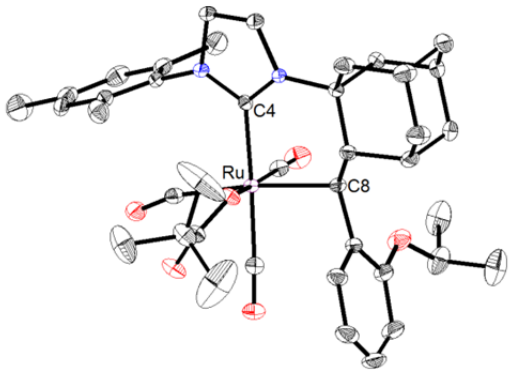
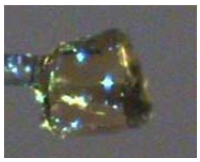


Table 1. Crystal data and structure refinement for 1.15 (CCDC 821420).

Empirical formula	$C_{40}H_{50}N_2O_6Ru$	
Formula weight	755.89	
Crystallization Solvent	Toluene/pentane	
Crystal Habit	Block	
Crystal size	0.29 x 0.27 x 0.24 mm^3	
Crystal color	Brown/yellow	

Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKa	
Data Collection Temperature	100(2) K	
q range for 9377 reflections used in lattice determination	4.990 to 80.929°	
Unit cell dimensions	a = 18.4243(7) Å	a= 90°
	b = 17.6260(7) Å	b= 90°
	c = 23.0612(10) Å	g = 90°
Volume	7489.0(5) $Å^3$	

Z	8
Crystal system	Orthorhombic
Space group	P *bca*
Density (calculated)	1.341 Mg/m^3
F(000)	3168
Data collection program	Bruker APEX2 v2009.7-0
q range for data collection	1.83 to 50.77°
Completeness to q = 50.77°	99.5 %
Index ranges	$-40 \leq h \leq 28$, $-38 \leq k \leq 38$, $-49 \leq l \leq 50$
Data collection scan type	ω scans; 12 settings
Data reduction program	Bruker SAINT-Plus v7.66A
Reflections collected	423400
Independent reflections	40410 [R_{int}= 0.0607]
Absorption coefficient	0.466 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.8963 and 0.8766

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)

Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	40410 / 0 / 450
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	2.102
Final R indices [I>2s(I), 22081 reflections]	R1 = 0.0405, *w*R2 = 0.0549
R indices (all data)	R1 = 0.0973, *w*R2 = 0.0571
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.003
Average shift/error	0.000
Largest diff. peak and hole	2.482 and -3.491 e.Å^{-3}

Special Refinement Details

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 1.15 (CCDC 821420). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}

Ru(1)	3782(1)	3301(1)	2518(1)	12(1)
O(1)	3738(1)	4440(1)	4018(1)	30(1)
O(2)	4223(1)	4942(1)	2616(1)	31(1)
O(3)	2892(1)	3646(1)	1406(1)	27(1)
O(4)	2231(1)	3676(1)	2948(1)	24(1)
O(5)	3642(1)	2118(1)	2538(1)	18(1)
O(6)	2491(1)	2142(1)	2239(1)	26(1)
N(1)	5321(1)	2590(1)	2500(1)	15(1)
N(2)	4988(1)	2960(1)	1638(1)	18(1)
C(1)	4801(1)	2949(1)	2203(1)	14(1)
C(2)	5891(1)	2283(1)	2106(1)	21(1)
C(3)	5731(1)	2680(1)	1540(1)	23(1)
C(4)	5430(1)	2521(1)	3134(1)	16(1)
C(5)	5929(1)	3179(1)	3325(1)	21(1)
C(6)	6126(1)	3093(1)	3968(1)	29(1)
C(7)	6520(1)	2341(1)	4062(1)	34(1)
C(8)	6021(1)	1682(1)	3892(1)	30(1)
C(9)	5819(1)	1760(1)	3250(1)	22(1)
C(10)	5424(1)	3106(1)	4331(1)	29(1)
C(11)	4934(1)	2444(1)	4140(1)	23(1)
C(12)	4717(1)	2511(1)	3490(1)	17(1)
C(13)	5327(1)	1697(1)	4256(1)	31(1)
C(14)	4628(1)	3324(1)	1167(1)	17(1)
C(15)	4755(1)	4093(1)	1061(1)	22(1)
C(16)	4402(1)	4428(1)	592(1)	28(1)
C(17)	3946(1)	4016(1)	231(1)	28(1)
C(18)	3853(1)	3250(1)	333(1)	24(1)
C(19)	4191(1)	2887(1)	796(1)	20(1)

C(20)	5264(1)	4550(1)	1435(1)	32(1)
C(21)	3554(1)	4398(1)	-264(1)	45(1)
C(22)	4060(1)	2061(1)	912(1)	29(1)
C(23)	4212(1)	3190(1)	3401(1)	16(1)
C(24)	3556(1)	3157(1)	3792(1)	19(1)
C(25)	3138(1)	2501(1)	3850(1)	24(1)
C(26)	2488(1)	2493(1)	4161(1)	32(1)
C(27)	2246(1)	3148(1)	4420(1)	37(1)
C(28)	2657(1)	3801(1)	4393(1)	34(1)
C(29)	3314(1)	3807(1)	4085(1)	24(1)
C(30)	3626(1)	5088(1)	4384(1)	35(1)
C(31)	4094(1)	5698(1)	4126(1)	45(1)
C(32)	3825(1)	4910(1)	5006(1)	50(1)
C(33)	4051(1)	4322(1)	2568(1)	19(1)
C(34)	3279(1)	3453(1)	1761(1)	20(1)
C(35)	2803(1)	3519(1)	2813(1)	18(1)
C(36)	3046(1)	1797(1)	2388(1)	18(1)
C(37)	3046(1)	925(1)	2418(1)	26(1)
C(38)	3804(1)	608(1)	2433(1)	86(1)
C(39)	2661(1)	603(1)	1893(1)	54(1)
C(40)	2617(1)	707(1)	2955(1)	93(1)

Table 3. Selected bond lengths [Å] and angles [°] for 1.15 (CCDC 821420).

Ru(1)-C(33)	1.8704(8)	Ru(1)-C(1)	2.1067(7)
Ru(1)-C(35)	1.9657(7)	Ru(1)-C(23)	2.1933(8)
Ru(1)-C(34)	1.9937(9)		
Ru(1)-O(5)	2.1007(5)		

C(33)-Ru(1)-C(35)	91.90(3)	C(34)-Ru(1)-C(1)	98.79(3)
C(33)-Ru(1)-C(34)	92.79(4)	O(5)-Ru(1)-C(1)	79.92(2)
C(35)-Ru(1)-C(34)	81.36(3)	C(33)-Ru(1)-C(23)	86.09(3)
C(33)-Ru(1)-O(5)	170.34(3)	C(35)-Ru(1)-C(23)	91.56(3)
C(35)-Ru(1)-O(5)	94.22(3)	C(34)-Ru(1)-C(23)	172.79(3)
C(34)-Ru(1)-O(5)	95.50(3)	O(5)-Ru(1)-C(23)	86.29(3)
C(33)-Ru(1)-C(1)	93.95(3)	C(1)-Ru(1)-C(23)	88.39(3)
C(35)-Ru(1)-C(1)	174.13(3)		

Table 4. Bond lengths [Å] and angles [°] for 1.15 (CCDC 821420).

Ru(1)-C(33)	1.8704(8)	N(2)-C(14)	1.4262(10)
Ru(1)-C(35)	1.9657(7)	N(2)-C(3)	1.4724(9)
Ru(1)-C(34)	1.9937(9)	C(2)-C(3)	1.5114(12)
Ru(1)-O(5)	2.1007(5)	C(4)-C(5)	1.5444(11)
Ru(1)-C(1)	2.1067(7)	C(4)-C(9)	1.5445(12)
Ru(1)-C(23)	2.1933(8)	C(4)-C(12)	1.5479(10)
O(1)-C(29)	1.3707(12)	C(5)-C(6)	1.5344(13)
O(1)-C(30)	1.4371(12)	C(6)-C(7)	1.5266(15)
O(2)-C(33)	1.1438(10)	C(6)-C(10)	1.5411(12)
O(3)-C(34)	1.1372(11)	C(7)-C(8)	1.5316(16)
O(4)-C(35)	1.1339(9)	C(8)-C(13)	1.5302(12)
O(5)-C(36)	1.2845(8)	C(8)-C(9)	1.5318(13)
O(6)-C(36)	1.2371(9)	C(10)-C(11)	1.5387(13)
N(1)-C(1)	1.3358(10)	C(11)-C(13)	1.5255(13)
N(1)-C(4)	1.4822(11)	C(11)-C(12)	1.5571(12)
N(1)-C(2)	1.4899(10)	C(12)-C(23)	1.5313(11)
N(2)-C(1)	1.3492(10)	C(14)-C(15)	1.3956(13)

C(14)-C(19)	1.4041(11)	C(35)-Ru(1)-C(1)	174.13(3)
C(15)-C(16)	1.3926(13)	C(34)-Ru(1)-C(1)	98.79(3)
C(15)-C(20)	1.5074(13)	O(5)-Ru(1)-C(1)	79.92(2)
C(16)-C(17)	1.3869(15)	C(33)-Ru(1)-C(23)	86.09(3)
C(17)-C(18)	1.3821(15)	C(35)-Ru(1)-C(23)	91.56(3)
C(17)-C(21)	1.5106(14)	C(34)-Ru(1)-C(23)	172.79(3)
C(18)-C(19)	1.3914(12)	O(5)-Ru(1)-C(23)	86.29(3)
C(19)-C(22)	1.5011(13)	C(1)-Ru(1)-C(23)	88.39(3)
C(23)-C(24)	1.5093(10)	C(29)-O(1)-C(30)	119.96(8)
C(24)-C(25)	1.3944(12)	C(36)-O(5)-Ru(1)	122.42(5)
C(24)-C(29)	1.4017(13)	C(1)-N(1)-C(4)	129.92(6)
C(25)-C(26)	1.3971(12)	C(1)-N(1)-C(2)	111.44(7)
C(26)-C(27)	1.3756(17)	C(4)-N(1)-C(2)	118.39(6)
C(27)-C(28)	1.3790(16)	C(1)-N(2)-C(14)	128.57(6)
C(28)-C(29)	1.4033(12)	C(1)-N(2)-C(3)	112.39(6)
C(30)-C(31)	1.5016(16)	C(14)-N(2)-C(3)	117.85(7)
C(30)-C(32)	1.5126(15)	N(1)-C(1)-N(2)	108.58(6)
C(36)-C(37)	1.5386(12)	N(1)-C(1)-Ru(1)	127.00(6)
C(37)-C(38)	1.5039(13)	N(2)-C(1)-Ru(1)	123.81(5)
C(37)-C(39)	1.5146(15)	N(1)-C(2)-C(3)	102.77(6)
C(37)-C(40)	1.5173(18)	N(2)-C(3)-C(2)	101.74(6)
		N(1)-C(4)-C(5)	107.50(6)
C(33)-Ru(1)-C(35)	91.90(3)	N(1)-C(4)-C(9)	107.79(7)
C(33)-Ru(1)-C(34)	92.79(4)	C(5)-C(4)-C(9)	109.06(6)
C(35)-Ru(1)-C(34)	81.36(3)	N(1)-C(4)-C(12)	114.13(6)
C(33)-Ru(1)-O(5)	170.34(3)	C(5)-C(4)-C(12)	111.23(7)
C(35)-Ru(1)-O(5)	94.22(3)	C(9)-C(4)-C(12)	106.99(7)
C(34)-Ru(1)-O(5)	95.50(3)	C(6)-C(5)-C(4)	110.05(7)
C(33)-Ru(1)-C(1)	93.95(3)	C(7)-C(6)-C(5)	109.52(8)

C(7)-C(6)-C(10)	109.57(9)	C(24)-C(23)-C(12)	112.13(7)
C(5)-C(6)-C(10)	108.91(7)	C(24)-C(23)-Ru(1)	105.62(5)
C(6)-C(7)-C(8)	109.78(7)	C(12)-C(23)-Ru(1)	114.44(5)
C(13)-C(8)-C(7)	110.34(9)	C(25)-C(24)-C(29)	117.11(7)
C(13)-C(8)-C(9)	108.96(7)	C(25)-C(24)-C(23)	122.07(8)
C(7)-C(8)-C(9)	108.95(8)	C(29)-C(24)-C(23)	120.69(8)
C(8)-C(9)-C(4)	110.99(8)	C(24)-C(25)-C(26)	122.08(10)
C(11)-C(10)-C(6)	109.03(8)	C(27)-C(26)-C(25)	119.52(10)
C(13)-C(11)-C(10)	109.09(7)	C(26)-C(27)-C(28)	120.12(8)
C(13)-C(11)-C(12)	110.81(8)	C(27)-C(28)-C(29)	120.24(10)
C(10)-C(11)-C(12)	111.59(7)	O(1)-C(29)-C(24)	115.46(7)
C(23)-C(12)-C(4)	115.87(7)	O(1)-C(29)-C(28)	123.64(9)
C(23)-C(12)-C(11)	110.18(7)	C(24)-C(29)-C(28)	120.79(9)
C(4)-C(12)-C(11)	107.07(6)	O(1)-C(30)-C(31)	104.66(9)
C(11)-C(13)-C(8)	108.41(8)	O(1)-C(30)-C(32)	110.96(9)
C(15)-C(14)-C(19)	121.50(8)	C(31)-C(30)-C(32)	112.60(10)
C(15)-C(14)-N(2)	119.47(7)	O(2)-C(33)-Ru(1)	177.88(9)
C(19)-C(14)-N(2)	118.88(8)	O(3)-C(34)-Ru(1)	164.08(7)
C(16)-C(15)-C(14)	117.92(8)	O(4)-C(35)-Ru(1)	174.98(8)
C(16)-C(15)-C(20)	120.56(9)	O(6)-C(36)-O(5)	124.39(8)
C(14)-C(15)-C(20)	121.52(8)	O(6)-C(36)-C(37)	120.29(7)
C(17)-C(16)-C(15)	121.82(9)	O(5)-C(36)-C(37)	115.30(6)
C(18)-C(17)-C(16)	118.95(9)	C(38)-C(37)-C(39)	108.21(11)
C(18)-C(17)-C(21)	120.27(10)	C(38)-C(37)-C(40)	111.80(13)
C(16)-C(17)-C(21)	120.77(11)	C(39)-C(37)-C(40)	108.22(11)
C(17)-C(18)-C(19)	121.58(8)	C(38)-C(37)-C(36)	111.91(7)
C(18)-C(19)-C(14)	118.12(8)	C(39)-C(37)-C(36)	109.74(8)
C(18)-C(19)-C(22)	120.72(8)	C(40)-C(37)-C(36)	106.91(9)
C(14)-C(19)-C(22)	121.08(8)		

Table 5. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for 1.15 (CCDC 821420). The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	110(1)	114(1)	146(1)	1(1)	13(1)	0(1)
O(1)	322(3)	256(3)	322(4)	-100(3)	77(3)	25(3)
O(2)	365(3)	170(3)	405(5)	-10(3)	81(3)	-43(2)
O(3)	210(3)	371(4)	235(4)	32(3)	-8(2)	75(2)
O(4)	180(2)	240(3)	291(4)	7(3)	43(2)	33(2)
O(5)	139(2)	132(2)	267(3)	2(2)	-27(2)	-11(2)
O(6)	162(2)	204(3)	418(4)	7(3)	-62(2)	-4(2)
N(1)	118(2)	196(3)	139(3)	-21(3)	9(2)	16(2)
N(2)	125(2)	251(4)	153(3)	-12(3)	6(2)	21(2)
C(1)	130(2)	150(3)	153(3)	-18(3)	-7(2)	-25(2)
C(2)	155(3)	288(4)	181(4)	-35(3)	9(3)	53(3)
C(3)	137(3)	373(5)	174(4)	-36(3)	18(3)	45(3)
C(4)	131(3)	206(4)	146(3)	4(3)	-1(2)	3(2)
C(5)	155(3)	285(5)	182(4)	-20(3)	-2(2)	-41(3)
C(6)	200(3)	487(6)	178(4)	-54(4)	-31(3)	-64(3)
C(7)	193(3)	642(8)	195(5)	72(5)	-31(3)	44(4)
C(8)	220(3)	422(6)	262(5)	139(4)	27(3)	104(4)
C(9)	181(3)	246(4)	248(4)	51(3)	27(3)	43(3)
C(10)	240(4)	472(6)	147(4)	-36(4)	-23(3)	-11(4)
C(11)	194(3)	341(5)	164(4)	48(4)	24(3)	21(3)
C(12)	141(3)	183(4)	172(4)	16(3)	8(2)	-9(2)
C(13)	248(4)	418(6)	255(5)	152(4)	36(3)	65(4)

C(14)	149(3)	221(4)	131(3)	-13(3)	12(2)	18(3)
C(15)	232(3)	244(4)	189(4)	-13(3)	54(3)	-18(3)
C(16)	332(4)	251(5)	259(5)	48(4)	83(4)	39(4)
C(17)	254(4)	398(6)	188(4)	48(4)	28(3)	115(4)
C(18)	204(3)	371(5)	151(3)	-48(3)	-22(2)	68(3)
C(19)	172(3)	242(4)	174(4)	-50(3)	0(3)	29(3)
C(20)	386(5)	287(5)	289(5)	-27(4)	54(4)	-134(4)
C(21)	423(5)	605(9)	334(7)	173(6)	-33(5)	170(5)
C(22)	298(4)	239(5)	326(6)	-70(4)	-50(4)	-4(3)
C(23)	138(3)	180(4)	164(4)	-2(3)	23(2)	-17(2)
C(24)	145(3)	268(4)	158(4)	18(3)	10(2)	3(3)
C(25)	175(3)	311(5)	229(5)	72(4)	10(3)	-26(3)
C(26)	192(3)	477(6)	277(5)	158(5)	14(3)	-74(4)
C(27)	200(3)	653(8)	243(5)	108(5)	89(3)	37(4)
C(28)	255(4)	520(7)	246(5)	-38(5)	73(3)	102(4)
C(29)	204(3)	325(5)	204(4)	-15(4)	27(3)	43(3)
C(30)	505(6)	259(5)	285(5)	-64(4)	9(4)	140(4)
C(31)	767(8)	219(5)	364(7)	-27(5)	-34(6)	51(5)
C(32)	840(9)	369(6)	298(6)	-49(5)	-48(6)	-39(7)
C(33)	192(3)	173(3)	219(4)	0(3)	41(3)	0(2)
C(34)	162(3)	219(4)	218(4)	-3(3)	32(3)	24(3)
C(35)	186(3)	157(3)	198(4)	18(3)	6(3)	3(2)
C(36)	153(2)	164(3)	223(4)	-2(3)	-15(2)	-11(2)
C(37)	254(3)	147(3)	395(6)	9(4)	-67(4)	-33(3)
C(38)	384(5)	157(4)	2040(20)	-51(9)	-516(10)	69(4)
C(39)	623(7)	250(6)	733(10)	-172(6)	-347(7)	49(5)
C(40)	1900(20)	258(7)	636(12)	8(7)	474(13)	-342(10)

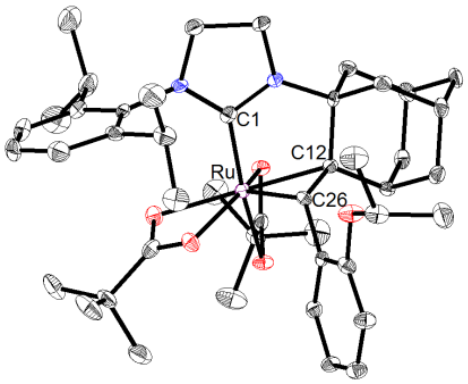
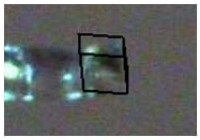


Table 1. Crystal data and structure refinement for 1.17 (CCDC 821618).

Empirical formula	$C_{45}H_{64}N_2O_5Ru$	
Formula weight	814.05	
Crystallization Solvent	THF	
Crystal Habit	Block	
Crystal size	0.10 x 0.07 x 0.07 mm^3	
Crystal color	Yellow	

Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKa	
Data Collection Temperature	100(2) K	
q range for 6383 reflections used in lattice determination	2.28 to 22.09°	
Unit cell dimensions	a = 10.1016(6) Å	a= 90°
	b = 19.2228(11) Å	b= 96.785(4)°
	c = 24.4253(15) Å	g = 90°
Volume	4709.7(5) $Å^3$	

Z	4
Crystal system	Monoclinic
Space group	P $2_1/c$
Density (calculated)	1.148 Mg/m^3
F(000)	1728
Data collection program	Bruker APEX2 v2009.7-0
q range for data collection	1.68 to 26.42°
Completeness to q = 26.42°	99.8 %
Index ranges	$-12 \leq h \leq 12$, $-24 \leq k \leq 24$, $-30 \leq l \leq 30$
Data collection scan type	ω scans; 10 settings
Data reduction program	Bruker SAINT-Plus v7.66A
Reflections collected	80574
Independent reflections	9657 [R_{int}= 0.1063]
Absorption coefficient	0.374 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9743 and 0.9636

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)

Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	9657 / 0 / 490
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.085
Final R indices [I>2s(I), 5961 reflections]	R1 = 0.0365, *w*R2 = 0.0463
R indices (all data)	R1 = 0.0792, *w*R2 = 0.0486
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	0.333 and -0.487 e.Å^{-3}

Special Refinement Details

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

The crystal contains disordered solvent which was accounted for by solvent flattening. The program SQUEEZE[1] was used and accounted for a total of 90 electrons in a void of 401 Å^3.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 1.17 (CCDC 821618). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

[1] SQUEEZE - Sluis, P. v.d.; Spek, A. L. Acta Crystallogr., Sect A 1990, 46, 194-201.

	x	y	z	U_{eq}
Ru(1)	8282(1)	1643(1)	1205(1)	13(1)
O(1)	11424(2)	2577(1)	119(1)	22(1)
O(2)	9625(2)	2225(1)	1742(1)	17(1)
O(3)	7912(2)	1750(1)	2066(1)	18(1)
O(4)	6906(2)	824(1)	1136(1)	15(1)
O(5)	8909(2)	584(1)	1547(1)	16(1)
N(1)	7011(2)	2407(1)	300(1)	14(1)
N(2)	6698(2)	2994(1)	1040(1)	16(1)
C(1)	7255(3)	2411(1)	854(1)	14(1)
C(2)	6256(3)	3001(1)	64(1)	18(1)
C(3)	5999(3)	3398(2)	585(1)	21(1)
C(4)	7421(3)	1806(1)	-8(1)	13(1)
C(5)	7959(3)	2017(1)	-552(1)	16(1)
C(6)	8437(3)	1364(1)	-825(1)	17(1)
C(7)	7255(3)	868(1)	-959(1)	18(1)
C(8)	6706(3)	654(1)	-422(1)	17(1)
C(9)	6234(3)	1307(1)	-140(1)	16(1)
C(10)	7783(3)	289(1)	-31(1)	15(1)
C(11)	8956(3)	781(1)	111(1)	14(1)
C(12)	8562(3)	1466(1)	365(1)	12(1)
C(13)	9510(3)	988(1)	-435(1)	18(1)
C(14)	7028(3)	3329(2)	1565(1)	18(1)
C(15)	8088(3)	3814(1)	1615(1)	21(1)
C(16)	8295(3)	4181(1)	2103(1)	27(1)
C(17)	7534(3)	4069(2)	2524(1)	33(1)

C(18)	6526(3)	3574(1)	2477(1)	28(1)
C(19)	6246(3)	3196(2)	1993(1)	22(1)
C(20)	8947(3)	3943(1)	1155(1)	23(1)
C(21)	8793(3)	4688(1)	937(1)	36(1)
C(22)	10418(3)	3776(1)	1349(1)	28(1)
C(23)	5108(3)	2676(2)	1923(2)	29(1)
C(24)	3772(3)	3036(2)	1744(1)	44(1)
C(25)	4995(3)	2252(2)	2440(1)	41(1)
C(26)	9592(3)	1905(1)	630(1)	13(1)
C(27)	11023(3)	1715(1)	754(1)	13(1)
C(28)	11501(3)	1215(1)	1139(1)	16(1)
C(29)	12841(3)	1069(1)	1241(1)	18(1)
C(30)	13752(3)	1406(1)	958(1)	19(1)
C(31)	13310(3)	1907(1)	574(1)	20(1)
C(32)	11964(3)	2067(1)	480(1)	17(1)
C(33)	12269(3)	2968(1)	-196(1)	20(1)
C(34)	11472(3)	3626(1)	-369(1)	31(1)
C(35)	12609(3)	2557(1)	-684(1)	33(1)
C(36)	9045(3)	2039(1)	2161(1)	19(1)
C(37)	9773(3)	2106(1)	2734(1)	21(1)
C(38)	10607(3)	2767(1)	2777(1)	35(1)
C(39)	8807(3)	2097(2)	3159(1)	32(1)
C(40)	10700(3)	1471(1)	2806(1)	35(1)
C(41)	7706(3)	424(1)	1443(1)	16(1)
C(42)	7148(3)	-222(1)	1695(1)	17(1)
C(43)	7072(3)	-810(1)	1266(1)	32(1)
C(44)	5755(3)	-66(1)	1841(1)	30(1)
C(45)	8054(3)	-433(1)	2205(1)	32(1)

Table 3. Selected bond lengths [Å] and angles [°] for 1.17 (CCDC 821618).

Ru(1)-C(1)	1.944(3)	C(1)-Ru(1)-O(4)	102.74(10)
Ru(1)-O(4)	2.0945(18)	C(1)-Ru(1)-O(2)	98.28(10)
Ru(1)-O(2)	2.095(2)	O(4)-Ru(1)-O(2)	145.66(8)
Ru(1)-C(26)	2.102(3)	C(1)-Ru(1)-C(26)	82.44(11)
Ru(1)-C(12)	2.130(3)	O(4)-Ru(1)-C(26)	126.22(9)
Ru(1)-O(3)	2.1887(19)	O(2)-Ru(1)-C(26)	83.05(10)
Ru(1)-O(5)	2.2642(17)	C(1)-Ru(1)-C(12)	79.70(11)
Ru(1)-C(36)	2.491(3)	O(4)-Ru(1)-C(12)	87.96(9)
Ru(1)-C(41)	2.501(3)	O(2)-Ru(1)-C(12)	122.61(10)
		C(26)-Ru(1)-C(12)	39.60(10)
		C(1)-Ru(1)-O(3)	102.13(10)
		O(4)-Ru(1)-O(3)	87.73(7)
		O(2)-Ru(1)-O(3)	61.29(7)
		C(26)-Ru(1)-O(3)	144.33(10)
		C(12)-Ru(1)-O(3)	175.60(9)
		C(1)-Ru(1)-O(5)	163.20(10)
		O(4)-Ru(1)-O(5)	60.46(7)
		O(2)-Ru(1)-O(5)	96.68(7)
		C(26)-Ru(1)-O(5)	106.98(9)
		C(12)-Ru(1)-O(5)	98.54(8)
		O(3)-Ru(1)-O(5)	78.54(7)
		C(1)-Ru(1)-C(36)	105.79(11)
		O(4)-Ru(1)-C(36)	115.70(9)
		O(2)-Ru(1)-C(36)	31.13(8)
		C(26)-Ru(1)-C(36)	113.85(11)
		C(12)-Ru(1)-C(36)	152.91(11)

O(3)-Ru(1)-C(36)	30.60(8)	C(26)-Ru(1)-C(41)	124.22(10)
O(5)-Ru(1)-C(36)	83.46(8)	C(12)-Ru(1)-C(41)	97.75(10)
C(1)-Ru(1)-C(41)	133.43(11)	O(3)-Ru(1)-C(41)	78.06(8)
O(4)-Ru(1)-C(41)	31.05(8)	O(5)-Ru(1)-C(41)	29.88(8)
O(2)-Ru(1)-C(41)	120.35(9)	C(36)-Ru(1)-C(41)	97.03(10)

Table 4. Bond lengths [Å] and angles [°] for 1.17 (CCDC 821618).

Ru(1)-C(1)	1.944(3)	C(2)-C(3)	1.531(3)
Ru(1)-O(4)	2.0945(18)	C(4)-C(12)	1.529(4)
Ru(1)-O(2)	2.095(2)	C(4)-C(9)	1.539(4)
Ru(1)-C(26)	2.102(3)	C(4)-C(5)	1.548(4)
Ru(1)-C(12)	2.130(3)	C(5)-C(6)	1.525(3)
Ru(1)-O(3)	2.1887(19)	C(6)-C(13)	1.536(4)
Ru(1)-O(5)	2.2642(17)	C(6)-C(7)	1.533(4)
Ru(1)-C(36)	2.491(3)	C(7)-C(8)	1.539(4)
Ru(1)-C(41)	2.501(3)	C(8)-C(10)	1.532(4)
O(1)-C(32)	1.385(3)	C(8)-C(9)	1.536(3)
O(1)-C(33)	1.430(3)	C(10)-C(11)	1.523(4)
O(2)-C(36)	1.288(3)	C(11)-C(12)	1.528(3)
O(3)-C(36)	1.269(3)	C(11)-C(13)	1.557(4)
O(4)-C(41)	1.291(3)	C(12)-C(26)	1.434(4)
O(5)-C(41)	1.250(3)	C(14)-C(19)	1.405(4)
N(1)-C(1)	1.346(4)	C(14)-C(15)	1.415(4)
N(1)-C(4)	1.465(3)	C(15)-C(16)	1.379(4)
N(1)-C(2)	1.455(3)	C(15)-C(20)	1.518(4)
N(2)-C(1)	1.357(3)	C(16)-C(17)	1.373(4)
N(2)-C(14)	1.439(3)	C(17)-C(18)	1.388(4)
N(2)-C(3)	1.466(3)	C(18)-C(19)	1.390(4)

C(19)-C(23)	1.518(4)	C(1)-Ru(1)-C(12)	79.70(11)
C(20)-C(22)	1.539(4)	O(4)-Ru(1)-C(12)	87.96(9)
C(20)-C(21)	1.530(3)	O(2)-Ru(1)-C(12)	122.61(10)
C(23)-C(24)	1.534(4)	C(26)-Ru(1)-C(12)	39.60(10)
C(23)-C(25)	1.518(4)	C(1)-Ru(1)-O(3)	102.13(10)
C(26)-C(27)	1.487(4)	O(4)-Ru(1)-O(3)	87.73(7)
C(27)-C(32)	1.401(3)	O(2)-Ru(1)-O(3)	61.29(7)
C(27)-C(28)	1.390(4)	C(26)-Ru(1)-O(3)	144.33(10)
C(28)-C(29)	1.376(4)	C(12)-Ru(1)-O(3)	175.60(9)
C(29)-C(30)	1.376(3)	C(1)-Ru(1)-O(5)	163.20(10)
C(30)-C(31)	1.382(3)	O(4)-Ru(1)-O(5)	60.46(7)
C(31)-C(32)	1.386(4)	O(2)-Ru(1)-O(5)	96.68(7)
C(33)-C(35)	1.503(4)	C(26)-Ru(1)-O(5)	106.98(9)
C(33)-C(34)	1.531(3)	C(12)-Ru(1)-O(5)	98.54(8)
C(36)-C(37)	1.507(4)	O(3)-Ru(1)-O(5)	78.54(7)
C(37)-C(38)	1.520(4)	C(1)-Ru(1)-C(36)	105.79(11)
C(37)-C(39)	1.506(4)	O(4)-Ru(1)-C(36)	115.70(9)
C(37)-C(40)	1.536(4)	O(2)-Ru(1)-C(36)	31.13(8)
C(41)-C(42)	1.523(4)	C(26)-Ru(1)-C(36)	113.85(11)
C(42)-C(44)	1.522(4)	C(12)-Ru(1)-C(36)	152.91(11)
C(42)-C(45)	1.510(4)	O(3)-Ru(1)-C(36)	30.60(8)
C(42)-C(43)	1.536(4)	O(5)-Ru(1)-C(36)	83.46(8)
		C(1)-Ru(1)-C(41)	133.43(11)
C(1)-Ru(1)-O(4)	102.74(10)	O(4)-Ru(1)-C(41)	31.05(8)
C(1)-Ru(1)-O(2)	98.28(10)	O(2)-Ru(1)-C(41)	120.35(9)
O(4)-Ru(1)-O(2)	145.66(8)	C(26)-Ru(1)-C(41)	124.22(10)
C(1)-Ru(1)-C(26)	82.44(11)	C(12)-Ru(1)-C(41)	97.75(10)
O(4)-Ru(1)-C(26)	126.22(9)	O(3)-Ru(1)-C(41)	78.06(8)
O(2)-Ru(1)-C(26)	83.05(10)	O(5)-Ru(1)-C(41)	29.88(8)

C(36)-Ru(1)-C(41)	97.03(10)	C(10)-C(8)-C(7)	110.7(2)
C(32)-O(1)-C(33)	120.0(2)	C(9)-C(8)-C(7)	109.1(2)
C(36)-O(2)-Ru(1)	91.63(18)	C(8)-C(9)-C(4)	109.1(2)
C(36)-O(3)-Ru(1)	87.97(19)	C(8)-C(10)-C(11)	109.5(2)
C(41)-O(4)-Ru(1)	92.14(18)	C(10)-C(11)-C(12)	113.2(2)
C(41)-O(5)-Ru(1)	85.61(17)	C(10)-C(11)-C(13)	108.2(2)
C(1)-N(1)-C(4)	119.4(2)	C(12)-C(11)-C(13)	105.4(2)
C(1)-N(1)-C(2)	114.8(2)	C(26)-C(12)-C(4)	118.2(2)
C(4)-N(1)-C(2)	125.7(2)	C(26)-C(12)-C(11)	118.7(3)
C(1)-N(2)-C(14)	127.3(3)	C(4)-C(12)-C(11)	109.9(2)
C(1)-N(2)-C(3)	111.4(2)	C(26)-C(12)-Ru(1)	69.13(16)
C(14)-N(2)-C(3)	118.7(2)	C(4)-C(12)-Ru(1)	109.23(18)
N(1)-C(1)-N(2)	107.9(3)	C(11)-C(12)-Ru(1)	126.87(19)
N(1)-C(1)-Ru(1)	117.7(2)	C(6)-C(13)-C(11)	110.6(2)
N(2)-C(1)-Ru(1)	134.5(2)	C(19)-C(14)-C(15)	122.8(3)
N(1)-C(2)-C(3)	101.2(2)	C(19)-C(14)-N(2)	119.3(3)
N(2)-C(3)-C(2)	104.7(2)	C(15)-C(14)-N(2)	117.7(3)
N(1)-C(4)-C(12)	105.6(2)	C(16)-C(15)-C(14)	116.6(3)
N(1)-C(4)-C(9)	109.7(2)	C(16)-C(15)-C(20)	121.0(3)
C(12)-C(4)-C(9)	111.9(2)	C(14)-C(15)-C(20)	122.4(3)
N(1)-C(4)-C(5)	112.5(2)	C(17)-C(16)-C(15)	121.8(3)
C(12)-C(4)-C(5)	107.9(2)	C(16)-C(17)-C(18)	121.0(3)
C(9)-C(4)-C(5)	109.2(2)	C(17)-C(18)-C(19)	120.2(3)
C(6)-C(5)-C(4)	108.7(2)	C(18)-C(19)-C(14)	117.5(3)
C(13)-C(6)-C(5)	110.6(2)	C(18)-C(19)-C(23)	121.0(3)
C(13)-C(6)-C(7)	108.3(2)	C(14)-C(19)-C(23)	121.5(3)
C(5)-C(6)-C(7)	109.0(2)	C(15)-C(20)-C(22)	110.8(3)
C(8)-C(7)-C(6)	109.5(2)	C(15)-C(20)-C(21)	111.5(2)
C(10)-C(8)-C(9)	109.2(2)	C(22)-C(20)-C(21)	110.9(2)

C(19)-C(23)-C(24)	111.3(3)	C(38)-C(37)-C(40)	109.3(3)
C(19)-C(23)-C(25)	113.0(3)	C(39)-C(37)-C(40)	110.4(3)
C(24)-C(23)-C(25)	109.2(3)	O(5)-C(41)-O(4)	119.9(3)
C(12)-C(26)-C(27)	125.7(2)	O(5)-C(41)-C(42)	121.0(3)
C(12)-C(26)-Ru(1)	71.27(16)	O(4)-C(41)-C(42)	119.0(3)
C(27)-C(26)-Ru(1)	118.5(2)	O(5)-C(41)-Ru(1)	64.51(15)
C(32)-C(27)-C(28)	117.2(3)	O(4)-C(41)-Ru(1)	56.81(14)
C(32)-C(27)-C(26)	118.8(3)	C(42)-C(41)-Ru(1)	164.9(2)
C(28)-C(27)-C(26)	124.0(3)	C(44)-C(42)-C(45)	110.3(3)
C(29)-C(28)-C(27)	121.3(3)	C(44)-C(42)-C(41)	109.3(2)
C(30)-C(29)-C(28)	121.0(3)	C(45)-C(42)-C(41)	109.6(3)
C(29)-C(30)-C(31)	119.2(3)	C(44)-C(42)-C(43)	109.3(3)
C(32)-C(31)-C(30)	120.0(3)	C(45)-C(42)-C(43)	109.9(2)
O(1)-C(32)-C(31)	124.6(3)	C(41)-C(42)-C(43)	108.4(2)
O(1)-C(32)-C(27)	114.0(3)		
C(31)-C(32)-C(27)	121.4(3)		
O(1)-C(33)-C(35)	110.9(2)		
O(1)-C(33)-C(34)	104.7(2)		
C(35)-C(33)-C(34)	112.3(3)		
O(3)-C(36)-O(2)	117.4(3)		
O(3)-C(36)-C(37)	122.6(3)		
O(2)-C(36)-C(37)	119.7(3)		
O(3)-C(36)-Ru(1)	61.42(17)		
O(2)-C(36)-Ru(1)	57.23(16)		
C(37)-C(36)-Ru(1)	163.7(2)		
C(36)-C(37)-C(38)	110.0(3)		
C(36)-C(37)-C(39)	110.7(3)		
C(38)-C(37)-C(39)	111.1(3)		
C(36)-C(37)-C(40)	105.2(2)		

Table 5. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for 1.17 (CCDC 821618). The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	128(1)	130(1)	135(1)	-5(2)	3(1)	12(2)
O(1)	164(13)	227(12)	275(16)	123(11)	22(12)	-10(10)
O(2)	209(14)	151(11)	149(14)	-22(10)	-10(11)	-37(10)
O(3)	204(13)	167(12)	176(14)	-22(11)	21(11)	-16(10)
O(4)	133(12)	129(11)	172(14)	8(10)	-9(11)	8(9)
O(5)	104(12)	181(11)	196(14)	50(10)	1(11)	-8(9)
N(1)	170(16)	115(14)	137(17)	7(12)	8(13)	46(11)
N(2)	173(16)	119(13)	171(18)	-31(12)	-37(13)	63(11)
C(1)	93(18)	145(17)	170(20)	-12(15)	35(16)	-21(13)
C(2)	183(19)	169(17)	190(20)	22(15)	13(16)	74(14)
C(3)	182(18)	186(17)	240(20)	-56(18)	-41(15)	51(16)
C(4)	166(18)	118(18)	120(19)	-34(14)	24(15)	35(13)
C(5)	190(20)	122(16)	170(20)	18(15)	-16(16)	20(14)
C(6)	230(20)	166(17)	120(20)	8(14)	67(17)	4(14)
C(7)	280(20)	147(17)	110(20)	-44(14)	1(17)	24(14)
C(8)	174(19)	149(17)	170(20)	-40(15)	-6(16)	-47(14)
C(9)	140(18)	155(16)	170(20)	-10(15)	-14(16)	0(14)
C(10)	201(19)	98(16)	160(20)	-22(14)	40(16)	-22(14)
C(11)	156(18)	123(16)	120(20)	0(14)	-14(15)	21(13)
C(12)	129(18)	127(17)	100(19)	35(13)	26(15)	21(13)
C(13)	174(19)	149(17)	210(20)	-55(15)	30(17)	6(14)
C(14)	196(18)	158(16)	169(19)	-75(18)	-43(15)	104(17)
C(15)	250(20)	145(17)	190(20)	-24(16)	-75(17)	75(15)

C(16)	340(20)	161(18)	300(30)	-40(17)	-60(20)	42(16)
C(17)	480(30)	300(20)	210(20)	-136(18)	-50(20)	167(19)
C(18)	280(20)	290(20)	260(20)	-91(17)	62(19)	85(16)
C(19)	220(20)	230(20)	210(20)	-30(16)	22(17)	103(15)
C(20)	280(20)	131(17)	260(20)	8(16)	-38(18)	-19(15)
C(21)	460(30)	209(19)	390(30)	41(18)	-20(20)	47(17)
C(22)	270(20)	249(19)	330(30)	37(18)	20(20)	-63(16)
C(23)	180(20)	380(20)	330(30)	-103(19)	90(20)	27(17)
C(24)	270(20)	620(30)	420(30)	-150(20)	70(20)	73(19)
C(25)	310(20)	480(20)	430(30)	40(20)	60(20)	-66(19)
C(26)	167(19)	151(16)	77(19)	44(13)	12(15)	33(13)
C(27)	162(17)	105(16)	127(18)	-36(15)	5(14)	34(15)
C(28)	162(19)	145(17)	160(20)	-20(14)	13(16)	-6(14)
C(29)	200(20)	126(16)	190(20)	23(15)	-7(18)	58(14)
C(30)	142(19)	190(18)	230(20)	0(15)	-8(17)	-8(14)
C(31)	130(18)	220(18)	230(20)	28(16)	3(17)	-23(14)
C(32)	210(20)	141(17)	140(20)	12(15)	-13(16)	-18(14)
C(33)	166(19)	203(18)	230(20)	94(16)	27(17)	-62(15)
C(34)	320(20)	240(19)	360(30)	107(17)	30(20)	-34(16)
C(35)	350(20)	410(20)	230(20)	-56(19)	40(20)	0(18)
C(36)	230(20)	90(17)	240(20)	-19(16)	32(18)	52(15)
C(37)	270(20)	187(18)	150(20)	-28(16)	-69(17)	-5(15)
C(38)	430(30)	370(20)	220(20)	-29(18)	-120(20)	-129(18)
C(39)	380(30)	440(20)	140(20)	-31(18)	-12(19)	-61(18)
C(40)	440(20)	340(20)	230(20)	-12(17)	-100(20)	125(18)
C(41)	157(19)	162(17)	160(20)	-61(15)	23(17)	0(14)
C(42)	200(20)	158(17)	150(20)	11(15)	-24(17)	-6(14)
C(43)	380(20)	202(19)	380(30)	21(18)	60(20)	-47(17)
C(44)	300(20)	260(20)	350(30)	52(18)	100(20)	-49(16)

C(45)	320(20)	310(20)	320(30)	175(18)	-50(20)	-83(17)

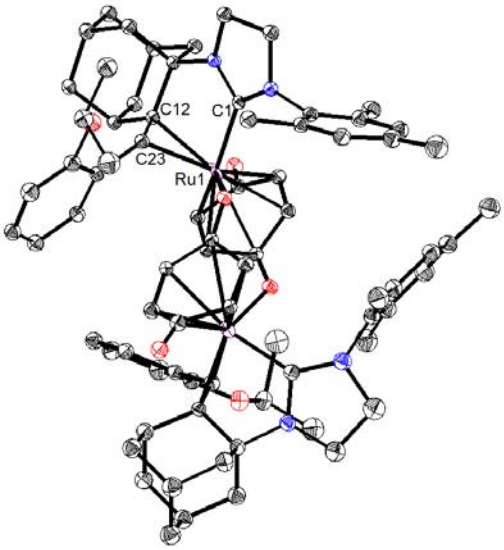
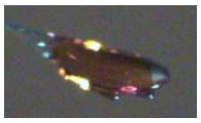


Table 1. Crystal data and structure refinement for 1.18 (CCDC 822993).

Empirical formula	$C_{76}H_{89}N_4O_6Ru_2 \bullet 1.5(C_6H_6O_2) \bullet 2.5(C_6H_6)$	
Formula weight	1717.08	
Crystallization Solvent	Benzene/hexene	
Crystal Habit	Plate	
Crystal size	0.39 x 0.11 x 0.02 mm^3	
Crystal color	Orange	

Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKa	
Data Collection Temperature	100(2) K	
q range for 9894 reflections used in lattice determination	2.23 to 26.01°	
Unit cell dimensions	a = 11.6013(8) Å	a= 85.265(5)°
	b = 13.9439(10) Å	b= 84.042(5)°

	c = 27.054(2) Å g = 71.743(4)°
Volume	4127.9(5) $Å^3$
Z	2
Crystal system	Triclinic
Space group	P-1
Density (calculated)	1.381 Mg/m^3
F(000)	1802
Data collection program	Bruker APEX2 v2009.7-0
q range for data collection	1.68 to 28.50°
Completeness to q = 28.50°	98.5 %
Index ranges	$-15 \leq h \leq 15$, $-18 \leq k \leq 18$, $-36 \leq l \leq 36$
Data collection scan type	ω scans; 2 settings
Data reduction program	Bruker SAINT-Plus v7.66A
Reflections collected	187612
Independent reflections	20621 [R_{int}= 0.1403]
Absorption coefficient	0.430 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9915 and 0.8503

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map

Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	20621 / 690 / 1049
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	2.999
Final R indices [I>2s(I), 14450 reflections]	R1 = 0.1156, *w*R2 = 0.1515
R indices (all data)	R1 = 0.1553, *w*R2 = 0.1538
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.003
Average shift/error	0.000
Largest diff. peak and hole	1.978 and -4.702 e.Å^{-3}

Special Refinement Details

The crystal was mounted on a fiber loop using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

The crystal is a twin with obvious edges for two components of stacked plates. It was not possible to account for this twinning in integration or refinement. Restraints were placed on the anisotropic placement parameters so as to approximate isotropic behavior.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1.18 (CCDC 822993). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Ru(1)	9340(1)	2672(1)	3648(1)	13(1)
Ru(2)	8341(1)	4160(1)	2073(1)	16(1)
O(1)	5629(4)	4459(3)	4324(2)	25(1)
O(2)	12454(4)	2095(3)	3948(2)	20(1)
O(3)	9753(3)	2931(3)	2374(1)	16(1)
O(4)	12181(4)	4427(3)	1839(2)	26(1)
O(5)	5217(4)	5699(3)	1906(2)	20(1)
O(6)	7855(3)	2897(3)	3187(1)	15(1)
N(1)	8529(4)	1618(4)	4528(2)	13(1)
N(2)	8037(4)	1001(4)	3902(2)	15(1)
N(3)	9125(5)	4071(4)	1014(2)	18(1)
N(4)	9306(5)	2531(4)	1271(2)	22(1)
C(1)	8610(5)	1628(4)	4030(2)	12(1)
C(2)	7765(6)	1029(5)	4776(2)	17(1)
C(3)	7617(5)	454(5)	4345(2)	17(1)
C(4)	8992(5)	2277(4)	4791(2)	12(1)
C(5)	10250(5)	1671(4)	4962(2)	15(1)
C(6)	10767(5)	2339(4)	5230(2)	16(1)
C(7)	9904(5)	2777(5)	5679(2)	18(1)
C(8)	8646(5)	3399(5)	5500(2)	18(1)
C(9)	8128(5)	2693(5)	5245(2)	17(1)
C(10)	8808(5)	4251(4)	5133(2)	15(1)
C(11)	9685(5)	3807(4)	4676(2)	14(1)
C(12)	9064(5)	3170(4)	4432(2)	13(1)

C(13)	10919(5)	3204(4)	4869(2)	16(1)
C(14)	7885(5)	617(4)	3444(2)	16(1)
C(15)	8789(6)	-205(5)	3242(2)	20(2)
C(16)	8485(6)	-726(5)	2884(2)	21(2)
C(17)	7331(6)	-432(5)	2718(2)	23(2)
C(18)	6464(6)	432(5)	2905(2)	21(2)
C(19)	6712(5)	963(5)	3266(2)	16(1)
C(20)	10069(6)	-571(5)	3405(2)	24(2)
C(21)	6996(7)	-1052(6)	2355(3)	37(2)
C(22)	5737(6)	1839(5)	3489(2)	21(2)
C(23)	8037(5)	3662(4)	4162(2)	14(1)
C(24)	7481(5)	4769(4)	4061(2)	15(1)
C(25)	8095(6)	5462(4)	3892(2)	17(1)
C(26)	7490(6)	6483(5)	3795(2)	19(1)
C(27)	6224(6)	6828(5)	3871(2)	19(2)
C(28)	5581(6)	6179(5)	4046(2)	25(2)
C(29)	6193(6)	5153(5)	4137(2)	20(2)
C(30)	4362(6)	4634(5)	4246(2)	24(2)
C(31)	4049(6)	3749(5)	4528(2)	28(2)
C(32)	4174(6)	4683(6)	3696(2)	34(2)
C(33)	11612(5)	2292(5)	3656(2)	15(1)
C(34)	11183(5)	1558(5)	3464(2)	16(1)
C(35)	10529(5)	1796(5)	3037(2)	15(1)
C(36)	10208(5)	2789(5)	2793(2)	14(1)
C(37)	10245(5)	3573(4)	3105(2)	12(1)
C(38)	10886(5)	3330(5)	3527(2)	14(1)
C(39)	8969(6)	3496(5)	1420(2)	18(1)
C(40)	9559(6)	3554(5)	555(2)	29(2)
C(41)	9638(7)	2471(5)	723(3)	35(2)

C(42)	8740(5)	5172(5)	1038(2)	17(1)
C(43)	7498(6)	5622(5)	836(2)	25(2)
C(44)	7062(6)	6773(5)	854(2)	27(2)
C(45)	7990(6)	7225(5)	556(2)	28(2)
C(46)	9232(6)	6773(5)	769(2)	24(2)
C(47)	9649(6)	5620(5)	727(2)	23(2)
C(48)	9107(6)	7027(5)	1313(2)	22(2)
C(49)	8174(6)	6574(5)	1618(2)	21(2)
C(50)	8696(5)	5428(5)	1579(2)	14(1)
C(51)	6943(6)	7036(5)	1399(2)	26(2)
C(52)	9654(6)	1566(5)	1543(2)	19(1)
C(53)	8870(6)	976(5)	1575(2)	21(2)
C(54)	9313(6)	-41(5)	1735(2)	23(2)
C(55)	10506(6)	-480(5)	1858(2)	24(2)
C(56)	11255(6)	135(5)	1836(2)	27(2)
C(57)	10861(6)	1154(5)	1669(2)	23(2)
C(58)	7589(6)	1409(5)	1422(3)	32(2)
C(59)	11010(6)	-1569(5)	2006(3)	31(2)
C(60)	11728(7)	1764(6)	1607(3)	34(2)
C(61)	9725(6)	4881(5)	1856(2)	17(1)
C(62)	10257(5)	5334(5)	2218(2)	16(1)
C(63)	9586(6)	5977(5)	2595(2)	18(1)
C(64)	10142(6)	6351(5)	2928(2)	20(2)
C(65)	11393(6)	6079(5)	2894(2)	24(2)
C(66)	12092(6)	5447(5)	2541(2)	28(2)
C(67)	11541(6)	5066(5)	2203(2)	19(2)
C(68)	13448(6)	3942(5)	1856(2)	22(2)
C(69)	13932(7)	3395(6)	1390(3)	35(2)
C(70)	13642(7)	3111(6)	2319(3)	39(2)

C(71)	6059(6)	5065(5)	2134(2)	19(1)
C(72)	6478(5)	4014(4)	2037(2)	15(1)
C(73)	7108(5)	3273(5)	2393(2)	17(1)
C(74)	7438(5)	3567(5)	2842(2)	13(1)
C(75)	7399(5)	4612(4)	2834(2)	13(1)
C(76)	6783(5)	5321(5)	2475(2)	18(1)
O(1A)	2905(4)	8862(4)	3921(2)	32(1)
O(2A)	4259(5)	7705(4)	1985(2)	36(1)
C(1A)	3268(6)	8586(5)	3436(2)	20(2)
C(2A)	3596(5)	9249(5)	3072(2)	19(2)
C(3A)	3929(6)	8937(5)	2607(3)	31(2)
C(4A)	3957(6)	7986(5)	2467(2)	22(2)
C(5A)	3628(6)	7333(5)	2837(2)	22(2)
C(6A)	3282(6)	7640(5)	3314(2)	20(2)
O(1B)	3763(4)	304(3)	4152(2)	25(1)
C(1B)	4367(5)	174(4)	4576(2)	14(1)
C(2B)	5099(5)	-794(5)	4706(2)	19(2)
C(3B)	4262(5)	969(5)	4868(2)	15(1)
C(1C)	2955(8)	6205(7)	821(3)	59(3)
C(2C)	3382(8)	7009(7)	830(3)	53(2)
C(3C)	3890(7)	7320(6)	385(3)	46(2)
C(4C)	3978(8)	6856(7)	-49(3)	53(2)
C(5C)	3545(9)	6014(7)	-39(4)	66(3)
C(6C)	2992(9)	5709(7)	400(3)	64(3)
C(1D)	4190(7)	1154(6)	372(3)	45(2)
C(2D)	3343(7)	727(6)	440(3)	44(2)

C(3D)	3393(7)	-139(5)	782(2)	32(2)
C(4D)	4443(7)	-468(6)	1060(3)	39(2)
C(5D)	5311(7)	25(6)	992(3)	41(2)
C(6D)	5174(8)	827(6)	652(3)	48(2)
C(1E)	9319(8)	-311(6)	375(3)	46(2)
C(2E)	8775(9)	453(7)	39(3)	57(2)
C(3E)	9482(8)	757(7)	-337(3)	53(2)

Table 3. Bond lengths [Å] and angles [°] for 1.18 (CCDC 822993).

Ru(1)-C(1)	2.060(6)
Ru(1)-O(6)	2.161(4)
Ru(1)-C(23)	2.167(6)
Ru(1)-C(35)	2.222(6)
Ru(1)-C(12)	2.244(6)
Ru(1)-C(38)	2.243(6)
Ru(1)-C(37)	2.246(5)
Ru(1)-C(34)	2.249(6)
Ru(1)-C(36)	2.440(6)
Ru(1)-C(33)	2.523(6)
Ru(2)-C(39)	2.022(6)
Ru(2)-O(3)	2.138(4)
Ru(2)-C(61)	2.158(6)
Ru(2)-C(73)	2.236(6)
Ru(2)-C(50)	2.243(6)
Ru(2)-C(72)	2.246(6)
Ru(2)-C(76)	2.262(6)
Ru(2)-C(75)	2.269(6)

Ru(2)-C(74)	2.431(6)
Ru(2)-C(71)	2.545(6)
O(1)-C(29)	1.366(7)
O(1)-C(30)	1.448(7)
O(2)-C(33)	1.269(6)
O(3)-C(36)	1.275(6)
O(4)-C(67)	1.377(7)
O(4)-C(68)	1.416(7)
O(5)-C(71)	1.268(7)
O(6)-C(74)	1.283(6)
N(1)-C(1)	1.338(7)
N(1)-C(4)	1.462(7)
N(1)-C(2)	1.468(7)
N(2)-C(1)	1.339(7)
N(2)-C(14)	1.438(7)
N(2)-C(3)	1.488(7)
N(3)-C(39)	1.338(7)
N(3)-C(42)	1.464(8)
N(3)-C(40)	1.451(8)
N(4)-C(39)	1.361(8)
N(4)-C(52)	1.440(8)
N(4)-C(41)	1.494(8)
C(2)-C(3)	1.521(8)
C(4)-C(12)	1.533(8)
C(4)-C(9)	1.533(8)
C(4)-C(5)	1.537(8)
C(5)-C(6)	1.518(8)
C(6)-C(13)	1.531(8)
C(6)-C(7)	1.528(8)

C(7)-C(8)	1.550(8)
C(8)-C(10)	1.529(8)
C(8)-C(9)	1.540(8)
C(10)-C(11)	1.554(8)
C(11)-C(12)	1.530(8)
C(11)-C(13)	1.536(8)
C(12)-C(23)	1.417(8)
C(14)-C(15)	1.393(8)
C(14)-C(19)	1.415(8)
C(15)-C(16)	1.394(8)
C(15)-C(20)	1.512(8)
C(16)-C(17)	1.383(8)
C(17)-C(18)	1.398(9)
C(17)-C(21)	1.515(9)
C(18)-C(19)	1.378(8)
C(19)-C(22)	1.499(8)
C(23)-C(24)	1.490(8)
C(24)-C(25)	1.393(8)
C(24)-C(29)	1.419(8)
C(25)-C(26)	1.393(8)
C(26)-C(27)	1.394(8)
C(27)-C(28)	1.370(8)
C(28)-C(29)	1.398(9)
C(30)-C(32)	1.519(8)
C(30)-C(31)	1.518(9)
C(33)-C(34)	1.424(8)
C(33)-C(38)	1.463(8)
C(34)-C(35)	1.408(8)
C(35)-C(36)	1.438(8)

C(36)-C(37)	1.449(8)
C(37)-C(38)	1.389(7)
C(40)-C(41)	1.518(9)
C(42)-C(43)	1.519(8)
C(42)-C(50)	1.527(8)
C(42)-C(47)	1.533(8)
C(43)-C(44)	1.527(9)
C(44)-C(51)	1.530(9)
C(44)-C(45)	1.540(9)
C(45)-C(46)	1.533(9)
C(46)-C(48)	1.525(8)
C(46)-C(47)	1.538(9)
C(48)-C(49)	1.552(8)
C(49)-C(50)	1.529(9)
C(49)-C(51)	1.529(8)
C(50)-C(61)	1.445(8)
C(52)-C(57)	1.403(8)
C(52)-C(53)	1.397(8)
C(53)-C(54)	1.397(9)
C(53)-C(58)	1.506(9)
C(54)-C(55)	1.390(9)
C(55)-C(56)	1.393(9)
C(55)-C(59)	1.483(9)
C(56)-C(57)	1.401(9)
C(57)-C(60)	1.497(9)
C(61)-C(62)	1.487(8)
C(62)-C(63)	1.413(8)
C(62)-C(67)	1.415(8)
C(63)-C(64)	1.381(8)

C(64)-C(65)	1.375(8)
C(65)-C(66)	1.370(9)
C(66)-C(67)	1.393(9)
C(68)-C(69)	1.494(9)
C(68)-C(70)	1.618(9)
C(71)-C(72)	1.430(8)
C(71)-C(76)	1.443(8)
C(72)-C(73)	1.427(8)
C(73)-C(74)	1.437(8)
C(74)-C(75)	1.442(8)
C(75)-C(76)	1.406(8)
O(1A)-C(1A)	1.382(7)
O(2A)-C(4A)	1.373(7)
C(1A)-C(6A)	1.381(9)
C(1A)-C(2A)	1.400(8)
C(2A)-C(3A)	1.343(9)
C(3A)-C(4A)	1.398(9)
C(4A)-C(5A)	1.403(8)
C(5A)-C(6A)	1.373(8)
O(1B)-C(1B)	1.375(7)
C(1B)-C(2B)	1.391(8)
C(1B)-C(3B)	1.383(8)
C(2B)-C(3B)#1	1.396(8)
C(3B)-C(2B)#1	1.396(8)
C(1C)-C(6C)	1.369(12)
C(1C)-C(2C)	1.364(11)
C(2C)-C(3C)	1.381(10)
C(3C)-C(4C)	1.368(10)
C(4C)-C(5C)	1.412(12)

C(5C)-C(6C)	1.391(11)
C(1D)-C(2D)	1.291(10)
C(1D)-C(6D)	1.371(10)
C(2D)-C(3D)	1.449(10)
C(3D)-C(4D)	1.429(10)
C(4D)-C(5D)	1.377(10)
C(5D)-C(6D)	1.367(10)
C(1E)-C(3E)#2	1.331(11)
C(1E)-C(2E)	1.377(11)
C(2E)-C(3E)	1.365(11)
C(3E)-C(1E)#2	1.331(11)

C(1)-Ru(1)-O(6)	83.34(19)
C(1)-Ru(1)-C(23)	81.0(2)
O(6)-Ru(1)-C(23)	86.94(18)
C(1)-Ru(1)-C(35)	102.8(2)
O(6)-Ru(1)-C(35)	86.40(18)
C(23)-Ru(1)-C(35)	171.9(2)
C(1)-Ru(1)-C(12)	77.6(2)
O(6)-Ru(1)-C(12)	122.93(18)
C(23)-Ru(1)-C(12)	37.4(2)
C(35)-Ru(1)-C(12)	150.1(2)
C(1)-Ru(1)-C(38)	148.0(2)
O(6)-Ru(1)-C(38)	128.09(18)
C(23)-Ru(1)-C(38)	104.1(2)
C(35)-Ru(1)-C(38)	76.6(2)
C(12)-Ru(1)-C(38)	87.6(2)
C(1)-Ru(1)-C(37)	167.8(2)
O(6)-Ru(1)-C(37)	92.30(17)

C(23)-Ru(1)-C(37)	110.2(2)
C(35)-Ru(1)-C(37)	65.4(2)
C(12)-Ru(1)-C(37)	114.2(2)
C(38)-Ru(1)-C(37)	36.04(19)
C(1)-Ru(1)-C(34)	95.3(2)
O(6)-Ru(1)-C(34)	121.52(18)
C(23)-Ru(1)-C(34)	150.9(2)
C(35)-Ru(1)-C(34)	36.7(2)
C(12)-Ru(1)-C(34)	113.5(2)
C(38)-Ru(1)-C(34)	64.7(2)
C(37)-Ru(1)-C(34)	77.2(2)
C(1)-Ru(1)-C(36)	132.2(2)
O(6)-Ru(1)-C(36)	74.33(17)
C(23)-Ru(1)-C(36)	137.4(2)
C(35)-Ru(1)-C(36)	35.5(2)
C(12)-Ru(1)-C(36)	149.5(2)
C(38)-Ru(1)-C(36)	63.4(2)
C(37)-Ru(1)-C(36)	35.71(19)
C(34)-Ru(1)-C(36)	64.1(2)
C(1)-Ru(1)-C(33)	115.9(2)
O(6)-Ru(1)-C(33)	145.27(17)
C(23)-Ru(1)-C(33)	123.0(2)
C(35)-Ru(1)-C(33)	62.0(2)
C(12)-Ru(1)-C(33)	90.5(2)
C(38)-Ru(1)-C(33)	35.1(2)
C(37)-Ru(1)-C(33)	62.68(19)
C(34)-Ru(1)-C(33)	34.10(19)
C(36)-Ru(1)-C(33)	71.47(19)
C(39)-Ru(2)-O(3)	84.3(2)

C(39)-Ru(2)-C(61)	82.1(2)
O(3)-Ru(2)-C(61)	86.63(19)
C(39)-Ru(2)-C(73)	100.9(2)
O(3)-Ru(2)-C(73)	84.78(18)
C(61)-Ru(2)-C(73)	170.6(2)
C(39)-Ru(2)-C(50)	77.6(2)
O(3)-Ru(2)-C(50)	123.41(18)
C(61)-Ru(2)-C(50)	38.3(2)
C(73)-Ru(2)-C(50)	151.0(2)
C(39)-Ru(2)-C(72)	92.7(2)
O(3)-Ru(2)-C(72)	120.17(18)
C(61)-Ru(2)-C(72)	152.2(2)
C(73)-Ru(2)-C(72)	37.1(2)
C(50)-Ru(2)-C(72)	113.9(2)
C(39)-Ru(2)-C(76)	145.0(2)
O(3)-Ru(2)-C(76)	129.28(19)
C(61)-Ru(2)-C(76)	106.2(2)
C(73)-Ru(2)-C(76)	76.5(2)
C(50)-Ru(2)-C(76)	88.3(2)
C(72)-Ru(2)-C(76)	63.9(2)
C(39)-Ru(2)-C(75)	165.9(2)
O(3)-Ru(2)-C(75)	93.25(18)
C(61)-Ru(2)-C(75)	111.7(2)
C(73)-Ru(2)-C(75)	65.1(2)
C(50)-Ru(2)-C(75)	114.9(2)
C(72)-Ru(2)-C(75)	76.5(2)
C(76)-Ru(2)-C(75)	36.2(2)
C(39)-Ru(2)-C(74)	131.3(2)
O(3)-Ru(2)-C(74)	73.84(17)

C(61)-Ru(2)-C(74)	137.3(2)
C(73)-Ru(2)-C(74)	35.54(19)
C(50)-Ru(2)-C(74)	150.1(2)
C(72)-Ru(2)-C(74)	64.2(2)
C(76)-Ru(2)-C(74)	63.6(2)
C(75)-Ru(2)-C(74)	35.5(2)
C(39)-Ru(2)-C(71)	113.3(2)
O(3)-Ru(2)-C(71)	144.51(17)
C(61)-Ru(2)-C(71)	124.8(2)
C(73)-Ru(2)-C(71)	62.4(2)
C(50)-Ru(2)-C(71)	91.2(2)
C(72)-Ru(2)-C(71)	34.0(2)
C(76)-Ru(2)-C(71)	34.3(2)
C(75)-Ru(2)-C(71)	62.0(2)
C(74)-Ru(2)-C(71)	71.52(19)
C(29)-O(1)-C(30)	119.7(5)
C(36)-O(3)-Ru(2)	131.5(4)
C(67)-O(4)-C(68)	120.3(5)
C(74)-O(6)-Ru(1)	131.8(3)
C(1)-N(1)-C(4)	121.9(5)
C(1)-N(1)-C(2)	114.2(5)
C(4)-N(1)-C(2)	123.1(5)
C(1)-N(2)-C(14)	135.5(5)
C(1)-N(2)-C(3)	111.7(5)
C(14)-N(2)-C(3)	112.0(4)
C(39)-N(3)-C(42)	119.7(5)
C(39)-N(3)-C(40)	116.5(5)
C(42)-N(3)-C(40)	123.4(5)
C(39)-N(4)-C(52)	132.0(5)

C(39)-N(4)-C(41)	112.6(5)
C(52)-N(4)-C(41)	113.8(5)
N(2)-C(1)-N(1)	107.9(5)
N(2)-C(1)-Ru(1)	134.7(4)
N(1)-C(1)-Ru(1)	116.9(4)
N(1)-C(2)-C(3)	100.9(5)
N(2)-C(3)-C(2)	103.0(5)
N(1)-C(4)-C(12)	107.7(4)
N(1)-C(4)-C(9)	111.0(5)
C(12)-C(4)-C(9)	108.4(5)
N(1)-C(4)-C(5)	109.1(5)
C(12)-C(4)-C(5)	111.5(5)
C(9)-C(4)-C(5)	109.3(5)
C(6)-C(5)-C(4)	110.4(5)
C(5)-C(6)-C(13)	108.8(5)
C(5)-C(6)-C(7)	110.2(5)
C(13)-C(6)-C(7)	109.3(5)
C(6)-C(7)-C(8)	109.2(5)
C(10)-C(8)-C(9)	110.3(5)
C(10)-C(8)-C(7)	108.9(5)
C(9)-C(8)-C(7)	108.7(5)
C(4)-C(9)-C(8)	108.6(5)
C(8)-C(10)-C(11)	110.4(5)
C(12)-C(11)-C(13)	114.3(5)
C(12)-C(11)-C(10)	105.6(5)
C(13)-C(11)-C(10)	107.4(5)
C(23)-C(12)-C(4)	117.4(5)
C(23)-C(12)-C(11)	119.2(5)
C(4)-C(12)-C(11)	108.9(5)

C(23)-C(12)-Ru(1)	68.3(3)
C(4)-C(12)-Ru(1)	108.9(4)
C(11)-C(12)-Ru(1)	129.5(4)
C(6)-C(13)-C(11)	109.8(5)
C(15)-C(14)-C(19)	121.3(6)
C(15)-C(14)-N(2)	120.2(5)
C(19)-C(14)-N(2)	117.3(5)
C(14)-C(15)-C(16)	118.2(6)
C(14)-C(15)-C(20)	123.0(6)
C(16)-C(15)-C(20)	118.8(6)
C(17)-C(16)-C(15)	121.7(6)
C(16)-C(17)-C(18)	118.7(6)
C(16)-C(17)-C(21)	120.8(6)
C(18)-C(17)-C(21)	120.5(6)
C(17)-C(18)-C(19)	121.8(6)
C(18)-C(19)-C(14)	118.1(6)
C(18)-C(19)-C(22)	120.7(5)
C(14)-C(19)-C(22)	121.1(5)
C(12)-C(23)-C(24)	127.6(5)
C(12)-C(23)-Ru(1)	74.2(4)
C(24)-C(23)-Ru(1)	124.1(4)
C(25)-C(24)-C(29)	116.8(5)
C(25)-C(24)-C(23)	126.6(5)
C(29)-C(24)-C(23)	116.6(5)
C(26)-C(25)-C(24)	122.4(6)
C(27)-C(26)-C(25)	119.0(6)
C(28)-C(27)-C(26)	120.7(6)
C(27)-C(28)-C(29)	120.0(6)
O(1)-C(29)-C(28)	123.8(6)

O(1)-C(29)-C(24)	115.0(5)
C(28)-C(29)-C(24)	121.1(6)
O(1)-C(30)-C(32)	111.4(5)
O(1)-C(30)-C(31)	104.3(5)
C(32)-C(30)-C(31)	112.2(6)
O(2)-C(33)-C(34)	125.0(5)
O(2)-C(33)-C(38)	122.0(5)
C(34)-C(33)-C(38)	112.7(5)
O(2)-C(33)-Ru(1)	142.3(4)
C(34)-C(33)-Ru(1)	62.3(3)
C(38)-C(33)-Ru(1)	61.9(3)
C(35)-C(34)-C(33)	120.5(5)
C(35)-C(34)-Ru(1)	70.6(3)
C(33)-C(34)-Ru(1)	83.6(4)
C(34)-C(35)-C(36)	122.3(6)
C(34)-C(35)-Ru(1)	72.7(3)
C(36)-C(35)-Ru(1)	80.6(4)
O(3)-C(36)-C(35)	119.6(5)
O(3)-C(36)-C(37)	125.8(5)
C(35)-C(36)-C(37)	113.6(5)
O(3)-C(36)-Ru(1)	132.9(4)
C(35)-C(36)-Ru(1)	63.9(3)
C(37)-C(36)-Ru(1)	64.8(3)
C(38)-C(37)-C(36)	120.7(5)
C(38)-C(37)-Ru(1)	71.8(3)
C(36)-C(37)-Ru(1)	79.5(3)
C(37)-C(38)-C(33)	121.7(6)
C(37)-C(38)-Ru(1)	72.1(3)
C(33)-C(38)-Ru(1)	83.0(3)

N(3)-C(39)-N(4)	105.9(5)
N(3)-C(39)-Ru(2)	119.0(4)
N(4)-C(39)-Ru(2)	135.1(5)
N(3)-C(40)-C(41)	101.8(5)
N(4)-C(41)-C(40)	103.1(6)
N(3)-C(42)-C(43)	109.4(5)
N(3)-C(42)-C(50)	108.5(5)
C(43)-C(42)-C(50)	110.9(5)
N(3)-C(42)-C(47)	110.7(5)
C(43)-C(42)-C(47)	108.8(5)
C(50)-C(42)-C(47)	108.4(5)
C(44)-C(43)-C(42)	111.1(5)
C(43)-C(44)-C(51)	108.0(5)
C(43)-C(44)-C(45)	110.2(6)
C(51)-C(44)-C(45)	109.4(6)
C(46)-C(45)-C(44)	109.2(5)
C(45)-C(46)-C(48)	108.9(6)
C(45)-C(46)-C(47)	109.0(5)
C(48)-C(46)-C(47)	110.0(5)
C(46)-C(47)-C(42)	109.4(5)
C(46)-C(48)-C(49)	110.4(5)
C(50)-C(49)-C(51)	113.8(5)
C(50)-C(49)-C(48)	105.9(5)
C(51)-C(49)-C(48)	108.0(5)
C(61)-C(50)-C(49)	118.7(5)
C(61)-C(50)-C(42)	117.4(5)
C(49)-C(50)-C(42)	109.1(5)
C(61)-C(50)-Ru(2)	67.7(3)
C(49)-C(50)-Ru(2)	130.6(4)

C(42)-C(50)-Ru(2)	108.5(4)
C(49)-C(51)-C(44)	109.5(6)
C(57)-C(52)-C(53)	121.2(6)
C(57)-C(52)-N(4)	118.9(5)
C(53)-C(52)-N(4)	118.4(5)
C(54)-C(53)-C(52)	118.5(6)
C(54)-C(53)-C(58)	120.3(6)
C(52)-C(53)-C(58)	121.2(6)
C(55)-C(54)-C(53)	122.0(6)
C(56)-C(55)-C(54)	118.1(6)
C(56)-C(55)-C(59)	119.1(6)
C(54)-C(55)-C(59)	122.8(6)
C(55)-C(56)-C(57)	122.0(6)
C(56)-C(57)-C(52)	118.1(6)
C(56)-C(57)-C(60)	120.3(6)
C(52)-C(57)-C(60)	121.5(6)
C(50)-C(61)-C(62)	124.8(5)
C(50)-C(61)-Ru(2)	74.0(3)
C(62)-C(61)-Ru(2)	122.8(4)
C(63)-C(62)-C(67)	116.8(5)
C(63)-C(62)-C(61)	125.4(5)
C(67)-C(62)-C(61)	117.8(6)
C(64)-C(63)-C(62)	122.4(6)
C(65)-C(64)-C(63)	118.7(6)
C(64)-C(65)-C(66)	121.6(6)
C(67)-C(66)-C(65)	120.1(6)
C(66)-C(67)-O(4)	123.5(6)
C(66)-C(67)-C(62)	120.4(6)
O(4)-C(67)-C(62)	116.0(5)

O(4)-C(68)-C(69)	109.0(5)
O(4)-C(68)-C(70)	108.1(5)
C(69)-C(68)-C(70)	107.9(6)
O(5)-C(71)-C(72)	122.5(6)
O(5)-C(71)-C(76)	124.9(6)
C(72)-C(71)-C(76)	112.3(5)
O(5)-C(71)-Ru(2)	143.0(4)
C(72)-C(71)-Ru(2)	61.4(3)
C(76)-C(71)-Ru(2)	62.0(3)
C(73)-C(72)-C(71)	121.3(6)
C(73)-C(72)-Ru(2)	71.1(3)
C(71)-C(72)-Ru(2)	84.5(4)
C(72)-C(73)-C(74)	120.9(6)
C(72)-C(73)-Ru(2)	71.8(3)
C(74)-C(73)-Ru(2)	79.7(3)
O(6)-C(74)-C(75)	125.0(5)
O(6)-C(74)-C(73)	120.0(5)
C(75)-C(74)-C(73)	114.6(5)
O(6)-C(74)-Ru(2)	134.1(4)
C(75)-C(74)-Ru(2)	66.1(3)
C(73)-C(74)-Ru(2)	64.8(3)
C(76)-C(75)-C(74)	120.9(5)
C(76)-C(75)-Ru(2)	71.7(3)
C(74)-C(75)-Ru(2)	78.4(3)
C(75)-C(76)-C(71)	121.8(6)
C(75)-C(76)-Ru(2)	72.2(4)
C(71)-C(76)-Ru(2)	83.6(4)
O(1A)-C(1A)-C(6A)	118.4(6)
O(1A)-C(1A)-C(2A)	121.3(6)

C(6A)-C(1A)-C(2A)	120.3(6)
C(3A)-C(2A)-C(1A)	118.4(6)
C(2A)-C(3A)-C(4A)	123.3(7)
O(2A)-C(4A)-C(3A)	121.9(6)
O(2A)-C(4A)-C(5A)	120.7(6)
C(3A)-C(4A)-C(5A)	117.4(6)
C(6A)-C(5A)-C(4A)	120.1(6)
C(1A)-C(6A)-C(5A)	120.6(6)
O(1B)-C(1B)-C(2B)	117.9(5)
O(1B)-C(1B)-C(3B)	122.1(5)
C(2B)-C(1B)-C(3B)	120.0(5)
C(1B)-C(2B)-C(3B)#1	120.3(6)
C(1B)-C(3B)-C(2B)#1	119.6(6)
C(6C)-C(1C)-C(2C)	123.8(9)
C(3C)-C(2C)-C(1C)	116.9(9)
C(4C)-C(3C)-C(2C)	122.9(8)
C(3C)-C(4C)-C(5C)	118.2(9)
C(4C)-C(5C)-C(6C)	119.9(9)
C(1C)-C(6C)-C(5C)	118.2(9)
C(2D)-C(1D)-C(6D)	120.0(8)
C(1D)-C(2D)-C(3D)	123.6(8)
C(2D)-C(3D)-C(4D)	114.7(7)
C(5D)-C(4D)-C(3D)	120.4(7)
C(6D)-C(5D)-C(4D)	119.7(8)
C(5D)-C(6D)-C(1D)	121.6(8)
C(3E)#2-C(1E)-C(2E)	121.1(8)
C(3E)-C(2E)-C(1E)	119.2(9)
C(1E)#2-C(3E)-C(2E)	119.6(9)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1

#2 -x+2,-y,-z

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for 1.18 (CCDC 822993). The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	43(2)	55(3)	287(3)	23(2)	-33(2)	-21(2)
Ru(2)	79(3)	131(3)	263(3)	18(2)	-39(2)	-32(2)
O(1)	220(13)	243(13)	279(14)	12(9)	-20(9)	-76(9)
O(2)	174(13)	204(13)	210(13)	-5(9)	-33(9)	-57(9)
O(3)	145(12)	152(12)	174(13)	6(9)	-13(9)	-46(9)
O(4)	236(13)	265(14)	270(14)	-22(9)	-33(9)	-77(9)
O(5)	185(13)	195(13)	208(13)	-3(9)	-27(9)	-53(9)
O(6)	133(12)	150(12)	170(13)	5(9)	-19(9)	-53(9)
N(1)	118(13)	119(14)	153(14)	-3(9)	-14(9)	-50(9)
N(2)	142(14)	145(14)	153(14)	-7(9)	-12(9)	-46(9)
N(3)	181(14)	169(15)	190(15)	-8(9)	-8(9)	-58(10)
N(4)	225(15)	216(15)	226(15)	-5(9)	-13(9)	-71(10)
C(1)	109(15)	116(15)	139(16)	-4(10)	-7(10)	-32(10)
C(2)	169(16)	166(16)	184(16)	2(10)	-8(10)	-64(10)
C(3)	171(16)	172(16)	184(17)	-3(10)	-13(10)	-61(10)
C(4)	118(15)	121(16)	133(16)	-5(10)	-13(10)	-41(10)
C(5)	150(16)	139(16)	166(16)	2(10)	-11(10)	-45(10)
C(6)	151(16)	151(16)	165(16)	0(10)	-22(10)	-50(10)
C(7)	184(16)	178(17)	194(17)	-1(10)	-14(10)	-64(10)
C(8)	173(16)	171(17)	183(17)	-8(10)	-16(10)	-58(10)

C(9)	163(16)	162(16)	178(16)	-3(10)	-15(10)	-55(10)
C(10)	151(16)	148(16)	165(16)	-7(10)	-17(10)	-47(10)
C(11)	131(15)	131(16)	146(16)	0(10)	-16(10)	-46(10)
C(12)	131(15)	127(16)	141(16)	-6(10)	-12(10)	-41(10)
C(13)	149(16)	158(16)	169(16)	-7(10)	-18(10)	-57(10)
C(14)	154(16)	148(16)	164(16)	6(10)	-4(10)	-54(10)
C(15)	192(17)	193(17)	207(17)	-6(10)	-14(10)	-63(10)
C(16)	209(17)	201(17)	224(17)	-9(10)	-9(10)	-71(10)
C(17)	231(17)	234(18)	242(18)	-17(10)	-17(10)	-82(10)
C(18)	209(17)	213(17)	220(17)	-9(10)	-21(10)	-74(10)
C(19)	162(16)	161(16)	175(16)	-3(10)	-11(10)	-55(10)
C(20)	232(18)	228(18)	249(18)	-3(10)	-17(10)	-72(10)
C(21)	370(20)	370(20)	380(20)	-24(10)	-31(10)	-125(11)
C(22)	203(17)	204(17)	214(17)	-10(10)	-18(10)	-62(10)
C(23)	137(16)	139(16)	153(16)	-5(10)	-11(10)	-49(10)
C(24)	144(16)	144(16)	154(16)	-6(10)	-15(10)	-43(10)
C(25)	165(16)	161(16)	176(16)	-6(10)	-20(10)	-49(10)
C(26)	188(16)	184(17)	200(17)	-6(10)	-19(10)	-60(10)
C(27)	189(17)	186(17)	202(17)	-8(10)	-15(10)	-53(10)
C(28)	234(18)	244(18)	256(18)	-10(10)	-23(10)	-69(10)
C(29)	194(17)	195(17)	205(17)	-3(10)	-18(10)	-58(10)
C(30)	231(18)	243(18)	259(18)	-13(10)	-21(10)	-76(10)
C(31)	266(18)	278(19)	292(19)	-13(10)	-18(10)	-87(11)
C(32)	340(20)	340(20)	350(20)	-21(10)	-29(10)	-101(11)
C(33)	141(16)	145(16)	153(16)	-2(10)	-15(10)	-41(10)
C(34)	149(16)	154(16)	160(16)	-7(10)	-9(10)	-46(10)
C(35)	149(16)	146(16)	160(16)	-4(10)	-9(10)	-49(10)
C(36)	137(16)	142(16)	149(16)	-11(10)	-10(10)	-45(10)
C(37)	108(15)	118(15)	134(16)	0(10)	-5(10)	-44(10)

C(38)	140(16)	140(16)	156(16)	-3(10)	-7(10)	-49(10)
C(39)	168(16)	175(17)	183(17)	-2(10)	-22(10)	-47(10)
C(40)	293(19)	282(19)	287(19)	-10(10)	-17(10)	-87(11)
C(41)	360(20)	340(20)	350(20)	-18(10)	-18(10)	-112(11)
C(42)	168(16)	168(16)	180(17)	-4(10)	-20(10)	-56(10)
C(43)	243(18)	253(18)	248(18)	-14(10)	-41(10)	-74(10)
C(44)	270(18)	272(19)	275(19)	-9(10)	-31(10)	-77(11)
C(45)	280(19)	282(19)	282(19)	-10(10)	-23(10)	-81(11)
C(46)	237(18)	238(18)	243(18)	-5(10)	-16(10)	-74(10)
C(47)	229(17)	236(18)	237(18)	-8(10)	-17(10)	-72(10)
C(48)	219(17)	216(17)	228(18)	-8(10)	-18(10)	-67(10)
C(49)	204(17)	203(17)	209(17)	-8(10)	-20(10)	-59(10)
C(50)	144(16)	135(16)	154(16)	0(10)	-8(10)	-50(10)
C(51)	252(18)	250(18)	256(18)	-4(10)	-21(10)	-71(10)
C(52)	188(17)	183(17)	191(17)	-7(10)	-10(10)	-59(10)
C(53)	209(17)	206(17)	217(17)	-11(10)	-20(10)	-62(10)
C(54)	221(17)	225(18)	237(18)	-9(10)	-17(10)	-73(10)
C(55)	235(18)	237(18)	242(18)	-9(10)	-21(10)	-72(10)
C(56)	269(19)	269(19)	277(19)	-13(10)	-25(10)	-80(11)
C(57)	227(17)	224(18)	237(18)	-14(10)	-17(10)	-76(10)
C(58)	320(20)	320(20)	330(20)	-21(10)	-35(10)	-102(11)
C(59)	305(19)	301(19)	310(20)	-9(10)	-19(10)	-93(11)
C(60)	340(20)	340(20)	360(20)	-29(10)	-30(10)	-117(11)
C(61)	165(16)	171(17)	178(17)	-10(10)	-12(10)	-55(10)
C(62)	154(16)	158(16)	165(16)	-1(10)	-15(10)	-52(10)
C(63)	174(16)	175(16)	189(17)	-7(10)	-19(10)	-59(10)
C(64)	202(17)	201(17)	210(17)	-12(10)	-15(10)	-67(10)
C(65)	234(18)	236(18)	243(18)	-16(10)	-25(10)	-75(11)
C(66)	270(18)	284(19)	291(19)	-20(10)	-29(10)	-91(11)

C(67)	185(17)	192(17)	203(17)	-9(10)	-15(10)	-66(10)
C(68)	202(17)	237(18)	241(18)	-41(10)	-28(10)	-71(10)
C(69)	340(20)	350(20)	360(20)	-26(10)	-31(10)	-111(11)
C(70)	380(20)	390(20)	400(20)	-24(10)	-38(10)	-118(11)
C(71)	183(16)	189(17)	193(17)	-7(10)	-17(10)	-56(10)
C(72)	142(16)	149(16)	161(16)	-10(10)	-15(10)	-56(10)
C(73)	164(16)	172(17)	180(17)	-6(10)	-11(10)	-54(10)
C(74)	125(15)	137(16)	146(16)	-6(10)	-8(10)	-49(10)
C(75)	121(15)	132(16)	140(16)	-11(10)	-12(10)	-39(10)
C(76)	177(16)	178(17)	186(17)	-5(10)	-10(10)	-58(10)
O(1A)	322(14)	313(14)	336(15)	-18(9)	-23(9)	-123(10)
O(2A)	362(15)	355(15)	367(15)	-10(9)	-14(9)	-106(10)
C(1A)	201(17)	201(17)	215(17)	-8(10)	-19(10)	-73(10)
C(2A)	188(17)	184(17)	208(17)	-12(10)	-17(10)	-66(10)
C(3A)	308(19)	315(19)	296(19)	2(10)	-23(10)	-86(11)
C(4A)	212(17)	225(17)	225(18)	-9(10)	-15(10)	-71(10)
C(5A)	223(17)	214(17)	237(18)	-7(10)	-18(10)	-75(10)
C(6A)	193(17)	192(17)	207(17)	-2(10)	-16(10)	-70(10)
O(1B)	251(13)	250(14)	266(14)	-17(9)	-41(9)	-76(9)
C(1B)	134(15)	142(16)	153(16)	-2(10)	-17(10)	-46(10)
C(2B)	190(17)	187(17)	205(17)	-17(10)	-15(10)	-69(10)
C(3B)	148(16)	147(16)	163(16)	-1(10)	-11(10)	-42(10)
C(1C)	590(30)	590(30)	590(30)	-23(10)	-43(10)	-179(12)
C(2C)	520(30)	530(30)	530(30)	-32(10)	-46(10)	-161(12)
C(3C)	450(20)	460(20)	460(20)	-30(10)	-42(10)	-144(12)
C(4C)	530(30)	520(30)	530(30)	-26(10)	-41(10)	-173(12)
C(5C)	670(30)	660(30)	670(30)	-42(10)	-57(10)	-215(13)

C(6C)	650(30)	640(30)	650(30)	-34(10)	-52(10)	-205(13)
C(1D)	450(20)	450(20)	450(20)	-16(10)	-36(10)	-138(12)
C(2D)	430(20)	430(20)	450(20)	-10(10)	-28(10)	-158(12)
C(3D)	320(20)	300(20)	330(20)	-19(10)	-22(10)	-96(11)
C(4D)	400(20)	390(20)	390(20)	-16(10)	-34(10)	-117(11)
C(5D)	400(20)	410(20)	410(20)	-15(10)	-40(10)	-122(11)
C(6D)	470(20)	480(20)	480(20)	-23(10)	-44(10)	-153(12)
C(1E)	460(20)	460(20)	460(20)	-21(10)	-34(10)	-145(12)
C(2E)	560(30)	570(30)	570(30)	-36(10)	-49(10)	-175(12)
C(3E)	530(30)	530(30)	530(30)	-23(10)	-49(10)	-167(12)

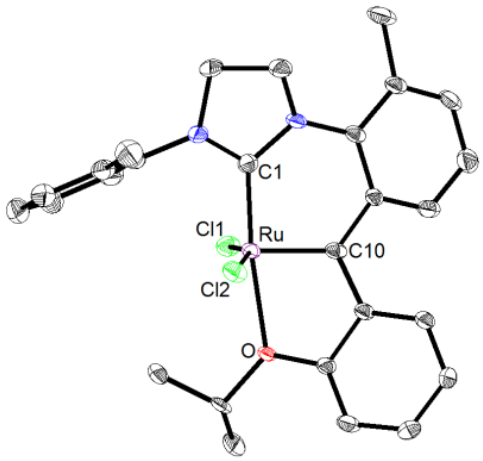


Table 1. Crystal data and structure refinement for 1.21 (CCDC 820386).

Empirical formula	$C_{27}H_{28}N_2OCl_2Ru$	
Formula weight	568.48	
Crystallization Solvent	Pentane/benzene	
Crystal Habit	Block	
Crystal size	0.21 x 0.16 x 0.11 mm^3	
Crystal color	Dark green	

Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKa	
Data Collection Temperature	100(2) K	
q range for 9861 reflections used in lattice determination	2.19 to 30.41°	
Unit cell dimensions	a = 29.5590(13) Å	a= 90°
	b = 10.0593(4) Å	b= 123.744(2)°
	c = 19.4668(9) Å	g = 90°

Volume	4813.1(4) $Å^3$
Z	8
Crystal system	Monoclinic
Space group	C 2/*c*
Density (calculated)	1.569 Mg/m^3
F(000)	2320
Data collection program	Bruker APEX2 v2009.7-0
q range for data collection	2.11 to 30.57°
Completeness to q = 30.57°	99.5 %
Index ranges	$-42 \leq h \leq 42$, $-14 \leq k \leq 14$, $-27 \leq l \leq 27$
Data collection scan type	ω scans; 16 settings
Data reduction program	Bruker SAINT-Plus v7.66A
Reflections collected	87437
Independent reflections	7362 [R_{int}= 0.0743]
Absorption coefficient	0.897 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9078 and 0.8340

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions

Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	7362 / 0 / 302
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.877
Final R indices [I>2s(I), 5532 reflections]	R1 = 0.0351, *w*R2 = 0.0531
R indices (all data)	R1 = 0.0556, *w*R2 = 0.0544
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	1.492 and -0.784 e.Å^{-3}

Special Refinement Details

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 1.21 (CCDC 820386). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Ru(1)	8809(1)	8497(1)	2901(1)	17(1)
Cl(1)	9133(1)	6973(1)	2362(1)	23(1)
Cl(2)	8766(1)	9651(1)	3910(1)	24(1)
O(1)	9524(1)	9799(2)	3266(1)	18(1)
N(1)	8053(1)	6872(2)	3034(1)	21(1)
N(2)	7628(1)	7869(2)	1824(1)	18(1)
C(1)	8136(1)	7652(2)	2549(1)	19(1)
C(2)	7486(1)	6434(3)	2622(1)	26(1)
C(3)	7199(1)	7488(2)	1965(2)	26(1)
C(4)	8495(1)	6248(2)	3775(1)	22(1)
C(5)	8847(1)	5427(2)	3709(2)	25(1)
C(6)	9280(1)	4836(3)	4416(2)	31(1)
C(7)	9355(1)	5060(3)	5167(2)	33(1)
C(8)	8999(1)	5852(3)	5227(2)	29(1)
C(9)	8560(1)	6471(3)	4529(1)	26(1)
C(10)	8189(1)	7341(3)	4615(2)	35(1)
C(11)	7555(1)	8587(2)	1148(1)	17(1)
C(12)	7084(1)	8392(2)	342(1)	21(1)
C(13)	7055(1)	9020(2)	-309(1)	24(1)
C(14)	7461(1)	9812(2)	-223(1)	25(1)
C(15)	7918(1)	10021(2)	563(1)	22(1)
C(16)	7967(1)	9455(2)	1255(1)	17(1)
C(17)	6619(1)	7469(3)	124(2)	32(1)
C(18)	8474(1)	9718(2)	2064(1)	17(1)
C(19)	8768(1)	10988(2)	2241(1)	16(1)

C(20)	8534(1)	12196(2)	1854(1)	18(1)
C(21)	8827(1)	13362(2)	2084(1)	22(1)
C(22)	9370(1)	13352(2)	2718(1)	24(1)
C(23)	9621(1)	12175(2)	3133(1)	21(1)
C(24)	9323(1)	11011(2)	2897(1)	17(1)
C(25)	10092(1)	9679(2)	3986(1)	20(1)
C(26)	10122(1)	8405(2)	4406(1)	24(1)
C(27)	10472(1)	9713(3)	3700(2)	29(1)

Table 3. Selected bond lengths [Å] and angles [°] for 1.21 (CCDC 820386).

Ru(1)-C(18)	1.830(2)	C(18)-Ru(1)-C(1)	92.23(10)
Ru(1)-C(1)	1.907(2)	C(18)-Ru(1)-O(1)	80.72(8)
Ru(1)-O(1)	2.2399(15)	C(1)-Ru(1)-O(1)	170.69(8)
Ru(1)-Cl(2)	2.3437(6)	C(18)-Ru(1)-Cl(2)	99.17(7)
Ru(1)-Cl(1)	2.3435(7)	C(1)-Ru(1)-Cl(2)	89.44(7)
		O(1)-Ru(1)-Cl(2)	85.73(4)
		C(18)-Ru(1)-Cl(1)	101.17(7)
		C(1)-Ru(1)-Cl(1)	98.77(7)
		O(1)-Ru(1)-Cl(1)	88.61(4)
		Cl(2)-Ru(1)-Cl(1)	157.69(2)

Table 4. Bond lengths [Å] and angles [°] for 1.21 (CCDC 820386).

Ru(1)-C(18)	1.830(2)	Ru(1)-Cl(2)	2.3437(6)
Ru(1)-C(1)	1.907(2)	Ru(1)-Cl(1)	2.3435(7)
Ru(1)-O(1)	2.2399(15)	O(1)-C(24)	1.372(2)

O(1)-C(25)	1.479(2)	C(23)-C(24)	1.382(3)
N(1)-C(1)	1.350(3)	C(25)-C(27)	1.505(3)
N(1)-C(2)	1.467(3)	C(25)-C(26)	1.496(3)
N(1)-C(4)	1.445(3)		
N(2)-C(11)	1.409(3)	C(18)-Ru(1)-C(1)	92.23(10)
N(2)-C(1)	1.393(3)	C(18)-Ru(1)-O(1)	80.72(8)
N(2)-C(3)	1.488(3)	C(1)-Ru(1)-O(1)	170.69(8)
C(2)-C(3)	1.507(3)	C(18)-Ru(1)-Cl(2)	99.17(7)
C(4)-C(5)	1.388(3)	C(1)-Ru(1)-Cl(2)	89.44(7)
C(4)-C(9)	1.390(3)	O(1)-Ru(1)-Cl(2)	85.73(4)
C(5)-C(6)	1.389(3)	C(18)-Ru(1)-Cl(1)	101.17(7)
C(6)-C(7)	1.370(3)	C(1)-Ru(1)-Cl(1)	98.77(7)
C(7)-C(8)	1.376(4)	O(1)-Ru(1)-Cl(1)	88.61(4)
C(8)-C(9)	1.399(3)	Cl(2)-Ru(1)-Cl(1)	157.69(2)
C(9)-C(10)	1.482(3)	C(24)-O(1)-C(25)	120.16(17)
C(11)-C(16)	1.417(3)	C(24)-O(1)-Ru(1)	107.18(12)
C(11)-C(12)	1.420(3)	C(25)-O(1)-Ru(1)	128.93(13)
C(12)-C(13)	1.376(3)	C(1)-N(1)-C(2)	112.77(19)
C(12)-C(17)	1.511(3)	C(1)-N(1)-C(4)	122.4(2)
C(13)-C(14)	1.369(3)	C(2)-N(1)-C(4)	122.76(19)
C(14)-C(15)	1.384(3)	C(11)-N(2)-C(1)	123.1(2)
C(15)-C(16)	1.393(3)	C(11)-N(2)-C(3)	126.94(17)
C(16)-C(18)	1.475(3)	C(1)-N(2)-C(3)	108.73(19)
C(18)-C(19)	1.475(3)	N(1)-C(1)-N(2)	106.8(2)
C(19)-C(24)	1.412(3)	N(1)-C(1)-Ru(1)	124.46(17)
C(19)-C(20)	1.395(3)	N(2)-C(1)-Ru(1)	128.05(18)
C(20)-C(21)	1.377(3)	N(1)-C(2)-C(3)	100.77(19)
C(21)-C(22)	1.378(3)	C(2)-C(3)-N(2)	101.64(18)
C(22)-C(23)	1.392(3)	C(5)-C(4)-C(9)	121.6(2)

C(5)-C(4)-N(1)	118.4(2)	C(21)-C(22)-C(23)	120.5(2)
C(9)-C(4)-N(1)	120.1(2)	C(22)-C(23)-C(24)	119.4(2)
C(6)-C(5)-C(4)	119.3(2)	O(1)-C(24)-C(23)	124.6(2)
C(5)-C(6)-C(7)	120.0(3)	O(1)-C(24)-C(19)	114.00(19)
C(8)-C(7)-C(6)	120.5(2)	C(23)-C(24)-C(19)	121.4(2)
C(7)-C(8)-C(9)	121.1(3)	O(1)-C(25)-C(27)	109.58(18)
C(8)-C(9)-C(10)	119.9(2)	O(1)-C(25)-C(26)	106.13(18)
C(8)-C(9)-C(4)	117.6(2)	C(27)-C(25)-C(26)	113.2(2)
C(10)-C(9)-C(4)	122.5(2)		
N(2)-C(11)-C(16)	120.46(19)		
N(2)-C(11)-C(12)	120.5(2)		
C(16)-C(11)-C(12)	118.9(2)		
C(13)-C(12)-C(11)	118.4(2)		
C(13)-C(12)-C(17)	116.3(2)		
C(11)-C(12)-C(17)	125.2(2)		
C(12)-C(13)-C(14)	123.5(2)		
C(13)-C(14)-C(15)	118.3(2)		
C(16)-C(15)-C(14)	121.4(2)		
C(15)-C(16)-C(11)	119.4(2)		
C(15)-C(16)-C(18)	117.3(2)		
C(11)-C(16)-C(18)	123.2(2)		
C(19)-C(18)-C(16)	121.5(2)		
C(19)-C(18)-Ru(1)	114.61(15)		
C(16)-C(18)-Ru(1)	123.85(17)		
C(24)-C(19)-C(20)	117.0(2)		
C(24)-C(19)-C(18)	117.6(2)		
C(20)-C(19)-C(18)	125.2(2)		
C(21)-C(20)-C(19)	122.2(2)		
C(22)-C(21)-C(20)	119.6(2)		

Table 5. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for 1.21 (CCDC 820386). The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	112(1)	146(1)	192(1)	0(1)	57(1)	1(1)
Cl(1)	218(3)	187(3)	272(3)	-26(2)	130(3)	-10(2)
Cl(2)	193(3)	244(4)	233(3)	-37(3)	93(3)	2(3)
O(1)	87(8)	152(9)	214(9)	-1(7)	30(7)	-2(7)
N(1)	133(10)	228(12)	255(11)	21(9)	94(9)	-16(8)
N(2)	95(10)	177(11)	218(11)	-2(8)	54(9)	-7(8)
C(1)	196(13)	152(13)	247(13)	-2(10)	133(11)	46(10)
C(2)	172(12)	282(15)	335(14)	18(13)	141(11)	-47(12)
C(3)	156(13)	266(15)	337(15)	14(11)	126(12)	-37(11)
C(4)	161(12)	199(15)	265(13)	36(10)	105(11)	-38(10)
C(5)	253(14)	235(15)	302(14)	0(11)	172(12)	-33(12)
C(6)	230(14)	277(16)	394(17)	62(13)	154(13)	54(12)
C(7)	274(16)	317(17)	313(16)	77(13)	109(13)	13(13)
C(8)	270(15)	317(16)	243(14)	0(11)	123(12)	-63(12)
C(9)	236(13)	234(14)	313(14)	-11(12)	162(11)	-29(12)
C(10)	340(17)	405(19)	331(16)	-2(13)	208(13)	25(14)
C(11)	132(11)	137(12)	227(12)	-29(10)	83(9)	14(10)
C(12)	129(11)	172(13)	255(13)	-36(11)	62(10)	6(11)
C(13)	140(12)	220(14)	204(13)	-25(10)	2(10)	15(10)
C(14)	233(14)	229(15)	198(13)	24(11)	67(11)	23(11)
C(15)	157(12)	191(14)	257(14)	-4(10)	85(11)	-13(10)

C(16)	114(11)	153(13)	196(12)	-21(10)	56(10)	20(9)
C(17)	189(14)	341(17)	290(15)	-57(12)	55(12)	-76(12)
C(18)	117(11)	180(13)	218(12)	-15(10)	90(10)	22(10)
C(19)	124(12)	155(12)	173(12)	-25(9)	72(10)	-22(9)
C(20)	119(12)	204(14)	185(12)	11(10)	60(10)	-2(10)
C(21)	223(13)	160(14)	227(12)	21(11)	95(10)	24(11)
C(22)	256(13)	158(14)	280(13)	-26(11)	131(11)	-52(11)
C(23)	142(12)	211(14)	216(13)	-37(10)	62(10)	-32(10)
C(24)	152(12)	137(12)	216(12)	16(9)	101(10)	29(9)
C(25)	81(11)	245(15)	175(12)	-18(10)	3(10)	-3(10)
C(26)	136(12)	226(14)	237(13)	32(11)	29(10)	29(11)
C(27)	142(13)	361(17)	307(15)	74(12)	86(11)	59(12)

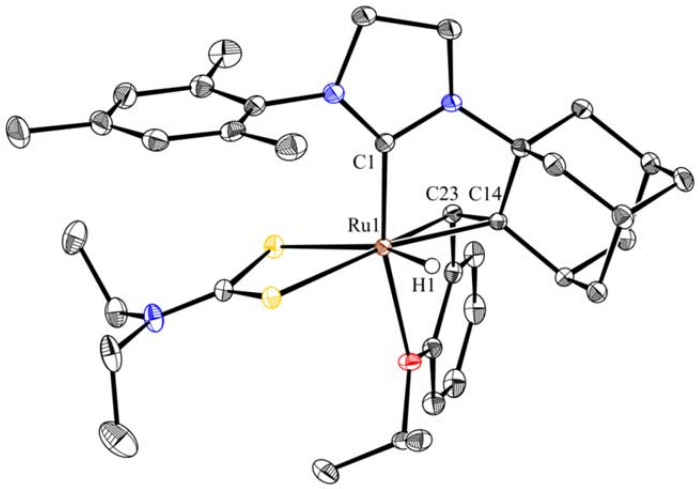


Table 1. Crystal Data and Structure Analysis Details for 1.22.

Empirical formula	C37 H51 N3 O Ru S2	
Formula weight	718.99	
Crystallization solvent	pentane/diethyl ether	
Crystal shape	block	
Crystal color	yellow	
Crystal size	0.2 x 0.33 x 0.47 mm	

Data Collection

Preliminary photograph(s)	rotation	
Type of diffractometer	Bruker APEX-II CCD	
Wavelength	0.71073 Å MoK	
Data collection temperature	100 K	
Theta range for 9862 reflections used in lattice determination	2.44 to 45.54°	
Unit cell dimensions	a = 8.6494(5) Å b = 10.4046(5) Å c = 19.5844(10) Å	a= 100.722(2)° b= 100.368(2)° g = 90.174(3)°
Volume	1702.21(16) $Å^3$	
Z	2	
Crystal system	triclinic	
Space group	P -1 (# 2)	
Density (calculated)	1.403 g/cm^3	

F(000)	756
Theta range for data collection	2.0 to 46.4°
Completeness to theta = 25.000°	99.9%
Index ranges	-17 £ h £ 17, -21 £ k £ 21, -39 £ l £ 39
Data collection scan type	ω scans
Reflections collected	275665
Independent reflections	29997 [R_{int}= 0.0441]
Reflections > 2s(I)	26227
Average s(I)/(net I)	0.0243
Absorption coefficient	0.62 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.9006

Structure Solution and Refinement

Primary solution method	dual
Hydrogen placement	difmap
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	29997 / 0 / 601
Treatment of hydrogen atoms	refall
Goodness-of-fit on F^2	1.51
Final R indices [I>2s(I), 26227 reflections]	R1 = 0.0307, wR2 = 0.0753
R indices (all data)	R1 = 0.0399, wR2 = 0.0782
Type of weighting scheme used	calc
Weighting scheme used	
Max shift/error	0.006
Average shift/error	0.000
Extinction coefficient	n/a
Largest diff. peak and hole	1.76 and -0.66 e·$Å^{-3}$

Programs Used

Cell refinement	SAINT V8.27B (Bruker-AXS, 2007)
Data collection	APEX2 2013.2-0 (Bruker-AXS, 2007)
Data reduction	SAINT V8.27B (Bruker-AXS, 2007)
Structure solution	SHELXT (Sheldrick, 2012)
Structure refinement	SHELXL-2013/2 (Sheldrick, 2013)

Special Refinement Details

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1.22. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Ru(1)	9594(1)	7120(1)	7275(1)	9(1)
S(1)	6807(1)	6585(1)	7301(1)	14(1)
S(2)	9512(1)	5382(1)	7964(1)	12(1)
O(1)	9016(1)	5680(1)	6184(1)	13(1)
N(1)	9845(1)	9003(1)	8685(1)	18(1)
N(2)	10586(1)	9777(1)	7823(1)	14(1)
N(3)	6556(1)	4483(1)	7889(1)	17(1)
C(1)	10026(1)	8665(1)	8002(1)	13(1)
C(2)	10245(1)	10391(1)	8985(1)	21(1)
C(3)	11117(1)	10801(1)	8444(1)	20(1)
C(4)	9187(1)	8225(1)	9094(1)	15(1)
C(5)	7590(1)	8297(1)	9134(1)	17(1)
C(6)	7012(1)	7568(1)	9569(1)	21(1)
C(7)	7982(1)	6799(1)	9964(1)	21(1)
C(8)	9568(1)	6775(1)	9923(1)	20(1)
C(9)	10197(1)	7489(1)	9497(1)	17(1)
C(10)	6518(1)	9155(1)	8740(1)	26(1)
C(11)	7330(2)	6032(1)	10433(1)	33(1)
C(12)	11922(1)	7502(1)	9473(1)	26(1)
C(13)	11335(1)	9579(1)	7202(1)	12(1)
C(14)	10483(1)	8382(1)	6696(1)	10(1)
C(15)	11323(1)	7983(1)	6070(1)	12(1)
C(16)	11120(1)	9129(1)	5664(1)	15(1)
C(17)	11899(1)	10389(1)	6143(1)	15(1)
C(18)	13655(1)	10171(1)	6359(1)	18(1)
C(19)	13875(1)	9037(1)	6766(1)	16(1)
C(20)	13104(1)	9357(1)	7417(1)	15(1)
C(21)	13078(1)	7777(1)	6297(1)	15(1)
C(22)	11152(1)	10738(1)	6810(1)	14(1)
C(23)	8790(1)	8352(1)	6566(1)	11(1)
C(24)	7849(1)	7600(1)	5900(1)	12(1)
C(25)	7986(1)	6240(1)	5706(1)	12(1)
C(26)	7116(1)	5534(1)	5080(1)	16(1)
C(27)	6061(1)	6180(1)	4644(1)	19(1)
C(28)	5893(1)	7517(1)	4827(1)	18(1)
C(29)	6790(1)	8215(1)	5452(1)	15(1)
C(30)	9507(1)	4349(1)	5962(1)	15(1)
C(31)	8331(1)	3368(1)	6082(1)	21(1)
C(32)	11134(1)	4242(1)	6385(1)	19(1)

C(33)	7502(1)	5374(1)	7744(1)	13(1)
C(34)	7170(1)	3473(1)	8282(1)	25(1)
C(35)	7374(2)	2195(1)	7797(1)	40(1)
C(36)	4839(1)	4494(1)	7668(1)	20(1)
C(37)	4088(1)	5390(1)	8209(1)	26(1)

Table 3. Bond lengths [Å] and angles [°] for 1.22.

Ru(1)-S(1)	2.4840(2)
Ru(1)-S(2)	2.45779(19)
Ru(1)-O(1)	2.3400(5)
Ru(1)-C(1)	1.9248(6)
Ru(1)-C(14)	2.1127(6)
Ru(1)-C(23)	2.0920(6)
Ru(1)-H(1)	1.574(13)
S(1)-C(33)	1.7108(7)
S(2)-C(33)	1.7136(7)
O(1)-C(25)	1.3839(8)
O(1)-C(30)	1.4596(8)
N(1)-C(1)	1.3566(9)
N(1)-C(2)	1.4691(10)
N(1)-C(4)	1.4225(10)
N(2)-C(1)	1.3793(9)
N(2)-C(3)	1.4623(9)
N(2)-C(13)	1.4617(9)
N(3)-C(33)	1.3372(9)
N(3)-C(34)	1.4609(11)
N(3)-C(36)	1.4707(10)
C(2)-H(2A)	0.977(13)
C(2)-H(2B)	0.968(14)
C(2)-C(3)	1.5257(12)
C(3)-H(3A)	0.939(14)
C(3)-H(3B)	0.966(15)
C(4)-C(5)	1.3988(11)
C(4)-C(9)	1.3971(11)
C(5)-C(6)	1.3940(11)
C(5)-C(10)	1.5028(12)
C(6)-H(6)	0.979(14)
C(6)-C(7)	1.3941(13)
C(7)-C(8)	1.3889(13)
C(7)-C(11)	1.5016(12)
C(8)-H(8)	0.992(15)
C(8)-C(9)	1.3916(12)
C(9)-C(12)	1.5011(13)
C(10)-H(10A)	0.97(2)
C(10)-H(10B)	0.93(2)
C(10)-H(10C)	0.950(18)
C(11)-H(11A)	0.95(2)
C(11)-H(11B)	1.01(2)
C(11)-H(11C)	0.93(2)

C(12)-H(12A)	0.911(19)
C(12)-H(12B)	0.927(18)
C(12)-H(12C)	0.931(19)
C(13)-C(14)	1.5320(9)
C(13)-C(20)	1.5423(10)
C(13)-C(22)	1.5391(9)
C(14)-C(15)	1.5286(9)
C(14)-C(23)	1.4398(9)
C(15)-H(15)	0.985(12)
C(15)-C(16)	1.5465(9)
C(15)-C(21)	1.5308(10)
C(16)-H(16A)	0.981(15)
C(16)-H(16B)	0.945(12)
C(16)-C(17)	1.5364(10)
C(17)-H(17)	0.952(13)
C(17)-C(18)	1.5312(11)
C(17)-C(22)	1.5443(10)
C(18)-H(18A)	0.965(16)
C(18)-H(18B)	1.000(15)
C(18)-C(19)	1.5353(11)
C(19)-H(19)	1.021(15)
C(19)-C(20)	1.5272(11)
C(19)-C(21)	1.5340(10)
C(20)-H(20A)	0.929(16)
C(20)-H(20B)	0.950(13)
C(21)-H(21A)	0.958(15)
C(21)-H(21B)	0.998(14)
C(22)-H(22A)	0.983(15)
C(22)-H(22B)	0.945(12)
C(23)-H(23)	0.914(14)
C(23)-C(24)	1.4857(9)
C(24)-C(25)	1.4070(9)
C(24)-C(29)	1.3939(9)
C(25)-C(26)	1.3918(9)
C(26)-H(26)	0.908(16)
C(26)-C(27)	1.3974(11)
C(27)-H(27)	1.008(14)
C(27)-C(28)	1.3849(13)
C(28)-H(28)	0.956(15)
C(28)-C(29)	1.3974(11)
C(29)-H(29)	0.921(13)
C(30)-H(30)	0.946(12)
C(30)-C(31)	1.5162(11)
C(30)-C(32)	1.5144(11)
C(31)-H(31A)	0.903(14)
C(31)-H(31B)	0.899(18)
C(31)-H(31C)	0.960(14)
C(32)-H(32A)	0.975(16)
C(32)-H(32B)	0.963(15)
C(32)-H(32C)	0.999(15)
C(34)-H(34A)	0.989(19)

C(34)-H(34B)	0.976(15)
C(34)-C(35)	1.5150(18)
C(35)-H(35A)	1.00(2)
C(35)-H(35B)	0.89(2)
C(35)-H(35C)	1.083(19)
C(36)-H(36A)	0.966(15)
C(36)-H(36B)	0.934(14)
C(36)-C(37)	1.5164(13)
C(37)-H(37A)	0.957(16)
C(37)-H(37B)	0.985(17)
C(37)-H(37C)	1.024(14)

S(1)-Ru(1)-H(1)	159.3(5)
S(2)-Ru(1)-S(1)	71.120(6)
S(2)-Ru(1)-H(1)	88.8(5)
O(1)-Ru(1)-S(1)	82.226(14)
O(1)-Ru(1)-S(2)	93.901(14)
O(1)-Ru(1)-H(1)	94.8(5)
C(1)-Ru(1)-S(1)	101.64(2)
C(1)-Ru(1)-S(2)	102.27(2)
C(1)-Ru(1)-O(1)	163.77(2)
C(1)-Ru(1)-C(14)	80.78(3)
C(1)-Ru(1)-C(23)	87.52(3)
C(1)-Ru(1)-H(1)	87.0(5)
C(14)-Ru(1)-S(1)	128.411(17)
C(14)-Ru(1)-S(2)	159.658(17)
C(14)-Ru(1)-O(1)	84.51(2)
C(14)-Ru(1)-H(1)	71.2(5)
C(23)-Ru(1)-S(1)	88.367(18)
C(23)-Ru(1)-S(2)	158.579(18)
C(23)-Ru(1)-O(1)	76.77(2)
C(23)-Ru(1)-C(14)	40.05(2)
C(23)-Ru(1)-H(1)	111.0(5)
C(33)-S(1)-Ru(1)	86.75(2)
C(33)-S(2)-Ru(1)	87.54(2)
C(25)-O(1)-Ru(1)	110.09(4)
C(25)-O(1)-C(30)	118.83(5)
C(30)-O(1)-Ru(1)	131.03(4)
C(1)-N(1)-C(2)	112.96(6)
C(1)-N(1)-C(4)	127.88(6)
C(4)-N(1)-C(2)	118.82(6)
C(1)-N(2)-C(3)	112.07(6)
C(1)-N(2)-C(13)	116.35(5)
C(13)-N(2)-C(3)	122.79(6)
C(33)-N(3)-C(34)	121.84(6)
C(33)-N(3)-C(36)	121.05(6)
C(34)-N(3)-C(36)	117.11(6)
N(1)-C(1)-Ru(1)	135.74(5)
N(1)-C(1)-N(2)	106.36(6)
N(2)-C(1)-Ru(1)	117.79(4)
N(1)-C(2)-H(2A)	110.0(7)

N(1)-C(2)-H(2B)	112.9(9)
N(1)-C(2)-C(3)	102.18(6)
H(2A)-C(2)-H(2B)	114.8(11)
C(3)-C(2)-H(2A)	109.0(8)
C(3)-C(2)-H(2B)	107.1(8)
N(2)-C(3)-C(2)	101.78(6)
N(2)-C(3)-H(3A)	109.7(9)
N(2)-C(3)-H(3B)	112.3(9)
C(2)-C(3)-H(3A)	115.2(9)
C(2)-C(3)-H(3B)	109.3(9)
H(3A)-C(3)-H(3B)	108.5(12)
C(5)-C(4)-N(1)	119.92(7)
C(9)-C(4)-N(1)	118.36(7)
C(9)-C(4)-C(5)	121.48(7)
C(4)-C(5)-C(10)	121.89(8)
C(6)-C(5)-C(4)	118.04(7)
C(6)-C(5)-C(10)	120.05(8)
C(5)-C(6)-H(6)	117.0(8)
C(5)-C(6)-C(7)	121.78(8)
C(7)-C(6)-H(6)	121.2(8)
C(6)-C(7)-C(11)	120.67(9)
C(8)-C(7)-C(6)	118.56(7)
C(8)-C(7)-C(11)	120.76(9)
C(7)-C(8)-H(8)	117.6(9)
C(7)-C(8)-C(9)	121.58(7)
C(9)-C(8)-H(8)	120.8(9)
C(4)-C(9)-C(12)	119.92(8)
C(8)-C(9)-C(4)	118.51(7)
C(8)-C(9)-C(12)	121.57(8)
C(5)-C(10)-H(10A)	113.1(12)
C(5)-C(10)-H(10B)	110.9(12)
C(5)-C(10)-H(10C)	111.1(11)
H(10A)-C(10)-H(10B)	110.3(17)
H(10A)-C(10)-H(10C)	102.4(16)
H(10B)-C(10)-H(10C)	108.7(16)
C(7)-C(11)-H(11A)	107.9(12)
C(7)-C(11)-H(11B)	111.2(11)
C(7)-C(11)-H(11C)	110.4(12)
H(11A)-C(11)-H(11B)	110.3(17)
H(11A)-C(11)-H(11C)	104.4(17)
H(11B)-C(11)-H(11C)	112.3(16)
C(9)-C(12)-H(12A)	104.5(12)
C(9)-C(12)-H(12B)	108.9(10)
C(9)-C(12)-H(12C)	112.1(12)
H(12A)-C(12)-H(12B)	110.5(16)
H(12A)-C(12)-H(12C)	105.4(15)
H(12B)-C(12)-H(12C)	114.9(16)
N(2)-C(13)-C(14)	106.08(5)
N(2)-C(13)-C(20)	110.13(5)
N(2)-C(13)-C(22)	113.04(5)
C(14)-C(13)-C(20)	111.55(5)

C(14)-C(13)-C(22)	107.52(5)
C(22)-C(13)-C(20)	108.51(5)
C(13)-C(14)-Ru(1)	110.04(4)
C(15)-C(14)-Ru(1)	126.70(4)
C(15)-C(14)-C(13)	110.08(5)
C(23)-C(14)-Ru(1)	69.21(3)
C(23)-C(14)-C(13)	117.12(5)
C(23)-C(14)-C(15)	118.69(5)
C(14)-C(15)-H(15)	108.5(7)
C(14)-C(15)-C(16)	105.36(5)
C(14)-C(15)-C(21)	112.92(5)
C(16)-C(15)-H(15)	110.7(7)
C(21)-C(15)-H(15)	110.0(7)
C(21)-C(15)-C(16)	109.22(5)
C(15)-C(16)-H(16A)	111.0(8)
C(15)-C(16)-H(16B)	109.4(7)
H(16A)-C(16)-H(16B)	104.6(11)
C(17)-C(16)-C(15)	109.89(6)
C(17)-C(16)-H(16A)	108.6(9)
C(17)-C(16)-H(16B)	113.3(7)
C(16)-C(17)-H(17)	108.6(8)
C(16)-C(17)-C(22)	110.71(6)
C(18)-C(17)-C(16)	108.47(6)
C(18)-C(17)-H(17)	109.8(8)
C(18)-C(17)-C(22)	109.57(6)
C(22)-C(17)-H(17)	109.6(8)
C(17)-C(18)-H(18A)	112.4(9)
C(17)-C(18)-H(18B)	110.3(9)
C(17)-C(18)-C(19)	109.78(6)
H(18A)-C(18)-H(18B)	108.2(12)
C(19)-C(18)-H(18A)	106.0(9)
C(19)-C(18)-H(18B)	110.0(8)
C(18)-C(19)-H(19)	111.5(8)
C(20)-C(19)-C(18)	109.26(6)
C(20)-C(19)-H(19)	107.4(8)
C(20)-C(19)-C(21)	108.22(6)
C(21)-C(19)-C(18)	110.02(6)
C(21)-C(19)-H(19)	110.4(8)
C(13)-C(20)-H(20A)	111.6(10)
C(13)-C(20)-H(20B)	108.4(8)
C(19)-C(20)-C(13)	110.75(6)
C(19)-C(20)-H(20A)	109.6(10)
C(19)-C(20)-H(20B)	113.1(8)
H(20A)-C(20)-H(20B)	103.2(12)
C(15)-C(21)-C(19)	109.69(6)
C(15)-C(21)-H(21A)	107.3(9)
C(15)-C(21)-H(21B)	109.6(8)
C(19)-C(21)-H(21A)	112.0(9)
C(19)-C(21)-H(21B)	110.3(8)
H(21A)-C(21)-H(21B)	107.9(12)
C(13)-C(22)-C(17)	108.45(5)

C(13)-C(22)-H(22A)	111.3(9)
C(13)-C(22)-H(22B)	107.2(7)
C(17)-C(22)-H(22A)	109.0(9)
C(17)-C(22)-H(22B)	112.3(7)
H(22A)-C(22)-H(22B)	108.7(11)
Ru(1)-C(23)-H(23)	114.4(9)
C(14)-C(23)-Ru(1)	70.75(3)
C(14)-C(23)-H(23)	117.7(9)
C(14)-C(23)-C(24)	121.53(5)
C(24)-C(23)-Ru(1)	111.02(4)
C(24)-C(23)-H(23)	113.6(9)
C(25)-C(24)-C(23)	121.03(6)
C(29)-C(24)-C(23)	121.17(6)
C(29)-C(24)-C(25)	117.80(6)
O(1)-C(25)-C(24)	115.05(6)
O(1)-C(25)-C(26)	123.77(6)
C(26)-C(25)-C(24)	121.17(6)
C(25)-C(26)-H(26)	120.7(10)
C(25)-C(26)-C(27)	119.54(7)
C(27)-C(26)-H(26)	119.7(10)
C(26)-C(27)-H(27)	117.9(8)
C(28)-C(27)-C(26)	120.40(7)
C(28)-C(27)-H(27)	121.7(8)
C(27)-C(28)-H(28)	120.4(9)
C(27)-C(28)-C(29)	119.39(7)
C(29)-C(28)-H(28)	120.0(9)
C(24)-C(29)-C(28)	121.68(7)
C(24)-C(29)-H(29)	118.1(8)
C(28)-C(29)-H(29)	120.2(8)
O(1)-C(30)-H(30)	106.2(7)
O(1)-C(30)-C(31)	110.02(6)
O(1)-C(30)-C(32)	107.10(6)
C(31)-C(30)-H(30)	111.0(7)
C(32)-C(30)-H(30)	110.1(7)
C(32)-C(30)-C(31)	112.16(7)
C(30)-C(31)-H(31A)	112.1(9)
C(30)-C(31)-H(31B)	113.0(11)
C(30)-C(31)-H(31C)	111.7(8)
H(31A)-C(31)-H(31B)	103.5(14)
H(31A)-C(31)-H(31C)	107.3(12)
H(31B)-C(31)-H(31C)	108.9(14)
C(30)-C(32)-H(32A)	112.7(9)
C(30)-C(32)-H(32B)	106.1(9)
C(30)-C(32)-H(32C)	108.5(8)
H(32A)-C(32)-H(32B)	112.7(12)
H(32A)-C(32)-H(32C)	104.6(13)
H(32B)-C(32)-H(32C)	112.3(12)
S(1)-C(33)-S(2)	114.13(4)
N(3)-C(33)-S(1)	122.64(5)
N(3)-C(33)-S(2)	123.21(5)
N(3)-C(34)-H(34A)	106.6(11)

N(3)-C(34)-H(34B)	110.8(9)
N(3)-C(34)-C(35)	112.12(9)
H(34A)-C(34)-H(34B)	101.9(14)
C(35)-C(34)-H(34A)	113.6(11)
C(35)-C(34)-H(34B)	111.3(9)
C(34)-C(35)-H(35A)	113.1(11)
C(34)-C(35)-H(35B)	112.0(12)
C(34)-C(35)-H(35C)	103.4(10)
H(35A)-C(35)-H(35B)	111.2(16)
H(35A)-C(35)-H(35C)	112.4(15)
H(35B)-C(35)-H(35C)	104.2(16)
N(3)-C(36)-H(36A)	108.8(9)
N(3)-C(36)-H(36B)	107.6(8)
N(3)-C(36)-C(37)	111.70(7)
H(36A)-C(36)-H(36B)	109.3(13)
C(37)-C(36)-H(36A)	107.9(9)
C(37)-C(36)-H(36B)	111.5(8)
C(36)-C(37)-H(37A)	109.3(10)
C(36)-C(37)-H(37B)	107.3(10)
C(36)-C(37)-H(37C)	109.8(8)
H(37A)-C(37)-H(37B)	112.2(14)
H(37A)-C(37)-H(37C)	107.9(13)
H(37B)-C(37)-H(37C)	110.4(13)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for 1.22. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	105(1)	92(1)	81(1)	14(1)	19(1)	2(1)
S(1)	117(1)	156(1)	149(1)	57(1)	30(1)	22(1)
S(2)	112(1)	136(1)	119(1)	42(1)	12(1)	2(1)
O(1)	164(2)	108(2)	103(2)	4(1)	8(1)	18(1)
N(1)	302(3)	145(2)	97(2)	-13(2)	63(2)	-52(2)
N(2)	196(2)	110(2)	103(2)	-7(2)	40(2)	-19(2)
N(3)	119(2)	202(3)	205(3)	96(2)	20(2)	-12(2)
C(1)	155(2)	126(2)	92(2)	10(2)	26(2)	-4(2)
C(2)	327(4)	158(3)	120(2)	-33(2)	61(3)	-42(3)
C(3)	296(4)	148(3)	136(3)	-30(2)	47(2)	-62(2)
C(4)	204(3)	152(2)	88(2)	6(2)	32(2)	-5(2)
C(5)	199(3)	180(3)	122(2)	20(2)	9(2)	8(2)
C(6)	214(3)	227(3)	177(3)	20(2)	49(2)	-33(3)
C(7)	317(4)	178(3)	145(3)	28(2)	54(3)	-51(3)
C(8)	296(4)	156(3)	131(2)	28(2)	9(2)	17(2)
C(9)	214(3)	165(3)	122(2)	-4(2)	22(2)	22(2)

C(10)	272(4)	258(4)	212(3)	49(3)	-23(3)	62(3)
C(11)	476(6)	275(4)	268(4)	93(3)	130(4)	-90(4)
C(12)	212(3)	276(4)	279(4)	-2(3)	36(3)	30(3)
C(13)	137(2)	107(2)	109(2)	14(2)	21(2)	-7(2)
C(14)	111(2)	95(2)	98(2)	16(2)	21(2)	6(2)
C(15)	133(2)	111(2)	120(2)	17(2)	43(2)	5(2)
C(16)	180(3)	147(2)	124(2)	43(2)	46(2)	2(2)
C(17)	181(3)	126(2)	162(2)	55(2)	51(2)	6(2)
C(18)	169(3)	150(3)	231(3)	49(2)	62(2)	-25(2)
C(19)	119(2)	161(3)	210(3)	48(2)	29(2)	-4(2)
C(20)	139(2)	149(2)	158(2)	31(2)	-6(2)	-22(2)
C(21)	131(2)	134(2)	205(3)	36(2)	65(2)	16(2)
C(22)	182(3)	104(2)	154(2)	27(2)	41(2)	8(2)
C(23)	114(2)	112(2)	108(2)	20(2)	23(2)	13(2)
C(24)	109(2)	145(2)	109(2)	37(2)	19(2)	1(2)
C(25)	132(2)	140(2)	99(2)	22(2)	15(2)	-7(2)
C(26)	175(3)	183(3)	113(2)	11(2)	6(2)	-32(2)
C(27)	166(3)	270(3)	120(2)	47(2)	-8(2)	-51(2)
C(28)	134(2)	268(3)	157(3)	97(2)	-11(2)	-21(2)
C(29)	120(2)	188(3)	157(2)	73(2)	12(2)	6(2)
C(30)	184(3)	116(2)	141(2)	-3(2)	36(2)	14(2)
C(31)	236(3)	144(3)	227(3)	33(2)	6(3)	-41(2)
C(32)	173(3)	166(3)	214(3)	16(2)	46(2)	48(2)
C(33)	114(2)	149(2)	121(2)	38(2)	24(2)	3(2)
C(34)	190(3)	313(4)	307(4)	210(3)	18(3)	-31(3)
C(35)	401(6)	244(4)	563(8)	192(5)	-22(5)	43(4)
C(36)	126(2)	256(3)	226(3)	81(3)	18(2)	-30(2)
C(37)	170(3)	391(5)	254(4)	89(3)	75(3)	19(3)

Table 5. Hydrogen coordinates (x 10^3) and isotropic displacement parameters (Å^{2}x 10^3) for 1.22.

	x	y	z	U_{iso}
H(1)	1143(2)	698(1)	736(1)	18(3)
H(2A)	1097(2)	1047(1)	944(1)	19(3)
H(2B)	933(2)	1092(1)	900(1)	24(3)
H(3A)	1087(2)	1162(1)	833(1)	25(3)
H(3B)	1224(2)	1080(1)	861(1)	26(3)
H(6)	588(2)	761(1)	958(1)	24(3)
H(8)	1025(2)	625(2)	1022(1)	32(4)
H(10A)	665(2)	1007(2)	896(1)	59(6)
H(10B)	548(2)	888(2)	869(1)	57(5)
H(10C)	676(2)	915(2)	828(1)	45(5)
H(11A)	670(2)	660(2)	1070(1)	61(6)
H(11B)	820(2)	568(2)	1076(1)	54(5)
H(11C)	663(2)	537(2)	1016(1)	56(5)
H(12A)	1235(2)	702(2)	980(1)	48(5)
H(12B)	1232(2)	836(2)	960(1)	42(4)

H(12C)	1213(2)	705(2)	904(1)	47(5)
H(15)	1080(1)	717(1)	577(1)	13(3)
H(16A)	1161(2)	895(1)	524(1)	28(3)
H(16B)	1004(1)	921(1)	549(1)	11(2)
H(17)	1176(2)	1108(1)	588(1)	16(3)
H(18A)	1420(2)	1092(2)	668(1)	32(4)
H(18B)	1416(2)	997(1)	593(1)	29(3)
H(19)	1504(2)	890(1)	694(1)	28(3)
H(20A)	1362(2)	1008(2)	772(1)	33(4)
H(20B)	1322(2)	869(1)	769(1)	20(3)
H(21A)	1351(2)	753(1)	588(1)	27(3)
H(21B)	1322(2)	704(1)	656(1)	23(3)
H(22A)	1168(2)	1154(1)	711(1)	28(3)
H(22B)	1006(1)	1088(1)	670(1)	13(3)
H(23)	831(2)	908(1)	676(1)	23(3)
H(26)	720(2)	465(2)	496(1)	36(4)
H(27)	544(2)	564(1)	419(1)	25(3)
H(28)	511(2)	795(1)	455(1)	29(3)
H(29)	668(2)	910(1)	558(1)	18(3)
H(30)	955(1)	426(1)	548(1)	11(2)
H(31A)	828(2)	344(1)	654(1)	25(3)
H(31B)	859(2)	253(2)	595(1)	42(4)
H(31C)	729(2)	348(1)	584(1)	24(3)
H(32A)	1185(2)	497(2)	638(1)	31(4)
H(32B)	1150(2)	340(1)	619(1)	28(3)
H(32C)	1105(2)	431(1)	689(1)	27(3)
H(34A)	645(2)	340(2)	861(1)	52(5)
H(34B)	815(2)	378(2)	861(1)	29(3)
H(35A)	640(2)	187(2)	744(1)	53(5)
H(35B)	774(2)	158(2)	804(1)	53(5)
H(35C)	833(2)	242(2)	755(1)	53(5)
H(36A)	440(2)	362(2)	762(1)	30(4)
H(36B)	464(2)	475(1)	723(1)	21(3)
H(37A)	440(2)	515(2)	866(1)	38(4)
H(37B)	294(2)	530(2)	804(1)	41(4)
H(37C)	448(2)	634(1)	825(1)	27(3)

Table 6. Torsion angles [°] for 1.22.

Ru(1)-S(1)-C(33)-S(2)	6.21(3)
Ru(1)-S(1)-C(33)-N(3)	-172.19(6)
Ru(1)-S(2)-C(33)-S(1)	-6.27(3)
Ru(1)-S(2)-C(33)-N(3)	172.12(6)
Ru(1)-O(1)-C(25)-C(24)	15.92(7)
Ru(1)-O(1)-C(25)-C(26)	-163.20(6)
Ru(1)-O(1)-C(30)-C(31)	90.58(7)
Ru(1)-O(1)-C(30)-C(32)	-31.57(8)
Ru(1)-C(14)-C(15)-C(16)	157.64(5)
Ru(1)-C(14)-C(15)-C(21)	-83.22(7)
Ru(1)-C(14)-C(23)-C(24)	-103.39(6)
Ru(1)-C(23)-C(24)-C(25)	-20.10(7)

Ru(1)-C(23)-C(24)-C(29)	159.15(5)
O(1)-C(25)-C(26)-C(27)	177.55(7)
N(1)-C(2)-C(3)-N(2)	19.77(9)
N(1)-C(4)-C(5)-C(6)	-176.78(7)
N(1)-C(4)-C(5)-C(10)	1.56(11)
N(1)-C(4)-C(9)-C(8)	177.07(6)
N(1)-C(4)-C(9)-C(12)	-1.87(10)
N(2)-C(13)-C(14)-Ru(1)	-28.30(6)
N(2)-C(13)-C(14)-C(15)	-172.45(5)
N(2)-C(13)-C(14)-C(23)	47.95(7)
N(2)-C(13)-C(20)-C(19)	175.30(5)
N(2)-C(13)-C(22)-C(17)	-176.74(6)
C(1)-N(1)-C(2)-C(3)	-14.20(10)
C(1)-N(1)-C(4)-C(5)	-93.47(10)
C(1)-N(1)-C(4)-C(9)	92.00(10)
C(1)-N(2)-C(3)-C(2)	-21.04(9)
C(1)-N(2)-C(13)-C(14)	32.46(8)
C(1)-N(2)-C(13)-C(20)	-88.39(7)
C(1)-N(2)-C(13)-C(22)	150.05(6)
C(2)-N(1)-C(1)-Ru(1)	-174.40(6)
C(2)-N(1)-C(1)-N(2)	1.62(9)
C(2)-N(1)-C(4)-C(5)	79.37(10)
C(2)-N(1)-C(4)-C(9)	-95.15(9)
C(3)-N(2)-C(1)-Ru(1)	-170.22(5)
C(3)-N(2)-C(1)-N(1)	12.91(9)
C(3)-N(2)-C(13)-C(14)	177.32(7)
C(3)-N(2)-C(13)-C(20)	56.47(9)
C(3)-N(2)-C(13)-C(22)	-65.09(9)
C(4)-N(1)-C(1)-Ru(1)	-1.21(14)
C(4)-N(1)-C(1)-N(2)	174.82(8)
C(4)-N(1)-C(2)-C(3)	171.93(7)
C(4)-C(5)-C(6)-C(7)	0.77(12)
C(5)-C(4)-C(9)-C(8)	2.63(10)
C(5)-C(4)-C(9)-C(12)	-176.31(7)
C(5)-C(6)-C(7)-C(8)	0.62(12)
C(5)-C(6)-C(7)-C(11)	179.53(8)
C(6)-C(7)-C(8)-C(9)	-0.42(12)
C(7)-C(8)-C(9)-C(4)	-1.17(11)
C(7)-C(8)-C(9)-C(12)	177.75(8)
C(9)-C(4)-C(5)-C(6)	-2.43(11)
C(9)-C(4)-C(5)-C(10)	175.91(7)
C(10)-C(5)-C(6)-C(7)	-177.60(8)
C(11)-C(7)-C(8)-C(9)	-179.33(8)
C(13)-N(2)-C(1)-Ru(1)	-21.69(8)
C(13)-N(2)-C(1)-N(1)	161.44(6)
C(13)-N(2)-C(3)-C(2)	-167.23(7)
C(13)-C(14)-C(15)-C(16)	-65.68(6)
C(13)-C(14)-C(15)-C(21)	53.46(7)
C(13)-C(14)-C(23)-Ru(1)	-102.55(5)
C(13)-C(14)-C(23)-C(24)	154.06(6)
C(14)-C(13)-C(20)-C(19)	57.78(7)

C(14)-C(13)-C(22)-C(17)	-60.01(7)
C(14)-C(15)-C(16)-C(17)	61.29(7)
C(14)-C(15)-C(21)-C(19)	-58.06(7)
C(14)-C(23)-C(24)-C(25)	59.61(9)
C(14)-C(23)-C(24)-C(29)	-121.13(7)
C(15)-C(14)-C(23)-Ru(1)	121.39(5)
C(15)-C(14)-C(23)-C(24)	18.00(9)
C(15)-C(16)-C(17)-C(18)	60.76(7)
C(15)-C(16)-C(17)-C(22)	-59.51(7)
C(16)-C(15)-C(21)-C(19)	58.82(7)
C(16)-C(17)-C(18)-C(19)	-60.43(8)
C(16)-C(17)-C(22)-C(13)	57.95(7)
C(17)-C(18)-C(19)-C(20)	-58.63(8)
C(17)-C(18)-C(19)-C(21)	60.04(8)
C(18)-C(17)-C(22)-C(13)	-61.65(7)
C(18)-C(19)-C(20)-C(13)	59.03(7)
C(18)-C(19)-C(21)-C(15)	-59.05(7)
C(20)-C(13)-C(14)-Ru(1)	91.63(5)
C(20)-C(13)-C(14)-C(15)	-52.52(7)
C(20)-C(13)-C(14)-C(23)	167.88(6)
C(20)-C(13)-C(22)-C(17)	60.79(7)
C(20)-C(19)-C(21)-C(15)	60.26(7)
C(21)-C(15)-C(16)-C(17)	-60.28(7)
C(21)-C(19)-C(20)-C(13)	-60.76(7)
C(22)-C(13)-C(14)-Ru(1)	-149.51(4)
C(22)-C(13)-C(14)-C(15)	66.34(6)
C(22)-C(13)-C(14)-C(23)	-73.26(7)
C(22)-C(13)-C(20)-C(19)	-60.49(7)
C(22)-C(17)-C(18)-C(19)	60.54(8)
C(23)-C(14)-C(15)-C(16)	73.20(7)
C(23)-C(14)-C(15)-C(21)	-167.66(6)
C(23)-C(24)-C(25)-O(1)	1.37(9)
C(23)-C(24)-C(25)-C(26)	-179.49(6)
C(23)-C(24)-C(29)-C(28)	-179.61(6)
C(24)-C(25)-C(26)-C(27)	-1.52(11)
C(25)-O(1)-C(30)-C(31)	-86.63(7)
C(25)-O(1)-C(30)-C(32)	151.22(6)
C(25)-C(24)-C(29)-C(28)	-0.33(10)
C(25)-C(26)-C(27)-C(28)	0.88(11)
C(26)-C(27)-C(28)-C(29)	0.00(11)
C(27)-C(28)-C(29)-C(24)	-0.27(11)
C(29)-C(24)-C(25)-O(1)	-177.91(6)
C(29)-C(24)-C(25)-C(26)	1.23(10)
C(30)-O(1)-C(25)-C(24)	-166.33(6)
C(30)-O(1)-C(25)-C(26)	14.55(10)
C(33)-N(3)-C(34)-C(35)	-96.20(10)
C(33)-N(3)-C(36)-C(37)	-86.62(9)
C(34)-N(3)-C(33)-S(1)	-178.63(7)
C(34)-N(3)-C(33)-S(2)	3.12(11)
C(34)-N(3)-C(36)-C(37)	92.39(10)
C(36)-N(3)-C(33)-S(1)	0.32(10)

C(36)-N(3)-C(33)-S(2)	-177.92(6)
C(36)-N(3)-C(34)-C(35)	84.80(10)

Symmetry transformations used to generate equivalent atoms:

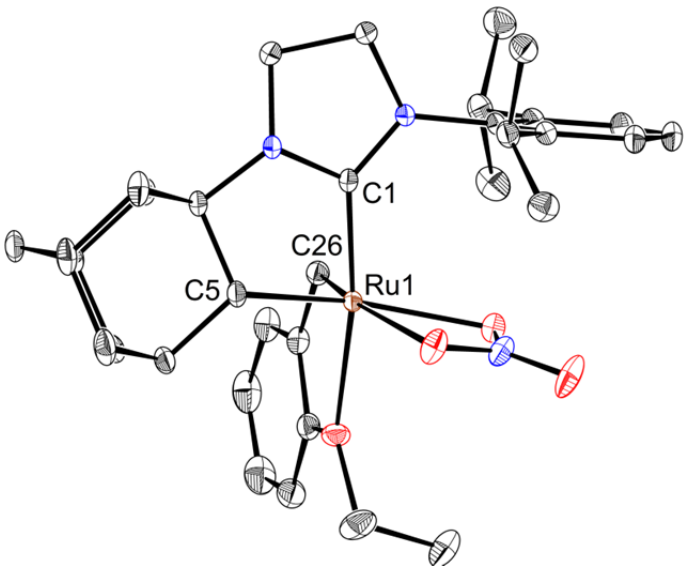


Table 1. Crystal Data and Structure Analysis Details for 1.35.

Empirical formula	C35 H47 N3 O4 Ru	
Formula weight	674.82	
Crystallization solvent	pentane/diethyl ether	
Crystal shape	blade	
Crystal color	purple	
Crystal size	0.07 x 0.12 x 0.41 mm	

Data Collection

Preliminary photograph(s)	matrix	
Type of diffractometer	Bruker APEX-II CCD	
Wavelength	0.71073 Å MoK	
Data collection temperature	100 K	
Theta range for 9845 reflections used in lattice determination	2.22 to 39.64°	
Unit cell dimensions	a = 10.5222(8) Å b = 19.5950(15) Å c = 15.8493(12) Å	a= 90° b= 99.340(2)° g = 90°
Volume	3224.5(4) Å^3	
Z	4	
Crystal system	monoclinic	
Space group	P 1 21/n 1 (# 14)	
Density (calculated)	1.390 g/cm^3	
F(000)	1416	

Theta range for data collection	1.7 to 41.2°
Completeness to theta = 25.000°	100.0%
Index ranges	-19 £ h £ 19, -36 £ k £ 35, -29 £ l £ 28
Data collection scan type	ω scans
Reflections collected	202446
Independent reflections	21156 [R_{int}= 0.0776]
Reflections > 2s(I)	15380
Average s(I)/(net I)	0.0493
Absorption coefficient	0.53 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.8876

Structure Solution and Refinement

Primary solution method	direct
Hydrogen placement	mixed
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	21156 / 0 / 606
Treatment of hydrogen atoms	mixed
Goodness-of-fit on F^2	1.16
Final R indices [I>2s(I), 15380 reflections]	R1 = 0.0362, wR2 = 0.0705
R indices (all data)	R1 = 0.0653, wR2 = 0.0782
Type of weighting scheme used	calc
Weighting scheme used	w=1/[^2^(Fo^2^)+(0.0300P)^2^] where P=(Fo^2^+2Fc^2^)/3
Max shift/error	0.003
Average shift/error	0.000
Extinction coefficient	n/a
Largest diff. peak and hole	1.04 and -0.78 e·$Å^{-3}$

Programs Used

Cell refinement	SAINT V8.34A (Bruker-AXS, 2007)
Data collection	APEX2 2013.12-0.0 (Bruker-AXS, 2007)
Data reduction	SAINT V8.34A (Bruker-AXS, 2007)
Structure solution	XT-2014/1 (Sheldrick, 2012)
Structure refinement	SHELXL-2014/2 (Sheldrick, 2014)
Graphics	DIAMOND 3 (Crystal Impact, 1999)

Special Refinement Details

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1.35. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Ru(1)	448(1)	1573(1)	3742(1)	11(1)
O(1)	2317(1)	973(1)	4214(1)	19(1)
O(2)	-544(1)	1340(1)	4915(1)	22(1)
O(3)	880(1)	2137(1)	4987(1)	18(1)
O(4)	23(1)	1893(1)	6120(1)	32(1)
N(1)	-1630(1)	1822(1)	2372(1)	13(1)
N(2)	-1433(1)	2734(1)	3178(1)	13(1)
N(3)	115(1)	1794(1)	5368(1)	19(1)
C(1)	-978(1)	2094(1)	3105(1)	11(1)
C(2)	-2311(1)	2347(1)	1813(1)	16(1)
C(3)	-2482(1)	2900(1)	2468(1)	16(1)
C(4)	-1202(1)	1163(1)	2100(1)	13(1)
C(5)	-481(1)	843(1)	2929(1)	14(1)
C(6)	93(1)	157(1)	2717(1)	20(1)
C(7)	976(1)	243(1)	2045(1)	22(1)
C(8)	214(1)	542(1)	1221(1)	18(1)
C(9)	-905(1)	66(1)	870(1)	20(1)
C(10)	-1798(1)	-10(1)	1537(1)	22(1)
C(11)	-2334(1)	698(1)	1728(1)	20(1)
C(12)	-328(1)	1241(1)	1419(1)	15(1)
C(13)	-1035(2)	-319(1)	2353(1)	26(1)
C(14)	-1188(1)	3155(1)	3930(1)	14(1)
C(15)	-1996(1)	3102(1)	4554(1)	15(1)
C(16)	-1742(1)	3534(1)	5266(1)	20(1)
C(17)	-734(1)	3995(1)	5353(1)	21(1)
C(18)	38(1)	4045(1)	4728(1)	19(1)
C(19)	-170(1)	3628(1)	4003(1)	15(1)
C(20)	-3138(1)	2615(1)	4474(1)	17(1)
C(21)	-3196(1)	2209(1)	5295(1)	23(1)
C(22)	-4413(1)	3000(1)	4221(1)	22(1)
C(23)	694(1)	3698(1)	3329(1)	18(1)
C(24)	2107(1)	3561(1)	3707(1)	27(1)
C(25)	542(2)	4399(1)	2900(1)	27(1)
C(26)	1545(1)	1917(1)	3045(1)	14(1)
C(27)	2856(1)	1659(1)	3125(1)	15(1)
C(28)	3725(1)	1868(1)	2592(1)	21(1)
C(29)	4955(1)	1589(1)	2680(1)	28(1)
C(30)	5337(1)	1117(1)	3315(1)	31(1)
C(31)	4507(1)	901(1)	3858(1)	26(1)

C(32)	3265(1)	1162(1)	3751(1)	17(1)
C(33)	2786(3)	530(1)	4949(1)	18(1)
C(33A)	2306(5)	425(3)	4871(4)	32(1)
C(34)	3526(3)	934(2)	5681(2)	30(1)
C(34A)	3145(8)	692(5)	5656(4)	64(3)
C(35)	1599(2)	200(1)	5182(1)	28(1)
C(35A)	2696(4)	-265(2)	4537(4)	52(2)

Table 3. Bond lengths [Å] and angles [°] for 1.35.

Ru(1)-O(1)	2.3105(8)
Ru(1)-O(2)	2.3214(8)
Ru(1)-O(3)	2.2423(8)
Ru(1)-C(1)	1.9542(10)
Ru(1)-C(5)	2.0616(10)
Ru(1)-C(26)	1.8490(10)
O(1)-C(32)	1.3822(13)
O(1)-C(33)	1.472(2)
O(1)-C(33A)	1.496(5)
O(2)-N(3)	1.2746(13)
O(3)-N(3)	1.2733(12)
O(4)-N(3)	1.2274(12)
N(1)-C(1)	1.3588(12)
N(1)-C(2)	1.4670(13)
N(1)-C(4)	1.4569(13)
N(2)-C(1)	1.3540(12)
N(2)-C(3)	1.4782(13)
N(2)-C(14)	1.4375(12)
C(2)-C(3)	1.5310(14)
C(2)-H(2A)	0.994(14)
C(2)-H(2B)	0.952(14)
C(3)-H(3A)	0.921(13)
C(3)-H(3B)	1.017(14)
C(4)-C(5)	1.5395(14)
C(4)-C(11)	1.5397(15)
C(4)-C(12)	1.5353(14)
C(5)-C(6)	1.5331(14)
C(5)-H(5)	0.933(17)
C(6)-C(7)	1.5314(17)
C(6)-C(13)	1.5454(18)
C(6)-H(6)	0.979(15)
C(7)-C(8)	1.5339(16)
C(7)-H(7A)	1.020(16)
C(7)-H(7B)	0.965(16)
C(8)-C(9)	1.5340(16)
C(8)-C(12)	1.5361(15)
C(8)-H(8)	0.926(15)
C(9)-C(10)	1.5310(16)
C(9)-H(9A)	0.993(16)
C(9)-H(9B)	0.962(16)

C(10)-C(11)	1.5445(17)
C(10)-C(13)	1.5324(19)
C(10)-H(10)	0.968(15)
C(11)-H(11A)	0.986(16)
C(11)-H(11B)	0.931(16)
C(12)-H(12A)	0.960(16)
C(12)-H(12B)	0.958(14)
C(13)-H(13A)	0.997(15)
C(13)-H(13B)	0.964(16)
C(14)-C(15)	1.4088(14)
C(14)-C(19)	1.4066(15)
C(15)-C(16)	1.4009(14)
C(15)-C(20)	1.5237(15)
C(16)-C(17)	1.3825(17)
C(16)-H(16)	0.891(15)
C(17)-C(18)	1.3822(17)
C(17)-H(17)	0.997(17)
C(18)-C(19)	1.3981(14)
C(18)-H(18)	1.016(15)
C(19)-C(23)	1.5179(16)
C(20)-C(21)	1.5350(16)
C(20)-C(22)	1.5349(16)
C(20)-H(20)	0.952(13)
C(21)-H(21A)	0.902(16)
C(21)-H(21B)	0.942(15)
C(21)-H(21C)	0.940(18)
C(22)-H(22A)	1.001(16)
C(22)-H(22B)	0.960(16)
C(22)-H(22C)	0.947(16)
C(23)-C(24)	1.5332(17)
C(23)-C(25)	1.5304(17)
C(23)-H(23)	0.977(14)
C(24)-H(24A)	0.952(17)
C(24)-H(24B)	0.949(17)
C(24)-H(24C)	0.996(16)
C(25)-H(25A)	0.954(16)
C(25)-H(25B)	0.965(19)
C(25)-H(25C)	0.955(18)
C(26)-C(27)	1.4555(15)
C(26)-H(26)	0.993(15)
C(27)-C(28)	1.4024(15)
C(27)-C(32)	1.4067(15)
C(28)-C(29)	1.3909(18)
C(28)-H(28)	0.935(15)
C(29)-C(30)	1.377(2)
C(29)-H(29)	0.908(18)
C(30)-C(31)	1.388(2)
C(30)-H(30)	0.969(17)
C(31)-C(32)	1.3877(16)
C(31)-H(31)	0.936(17)
C(33)-C(34)	1.512(4)

C(33)-C(35)	1.505(3)
C(33)-H(33)	0.98(2)
C(33A)-H(33A)	1.0000
C(33A)-C(34A)	1.498(10)
C(33A)-C(35A)	1.533(8)
C(34)-H(34A)	0.96(3)
C(34)-H(34B)	0.89(3)
C(34)-H(34C)	0.96(3)
C(34A)-H(34D)	0.9800
C(34A)-H(34E)	0.9800
C(34A)-H(34F)	0.9800
C(35)-H(35A)	0.97(3)
C(35)-H(35B)	0.99(3)
C(35)-H(35C)	0.95(3)
C(35A)-H(35D)	0.9800
C(35A)-H(35E)	0.9800
C(35A)-H(35F)	0.9800

O(1)-Ru(1)-O(2)	96.30(3)
O(3)-Ru(1)-O(1)	85.68(3)
O(3)-Ru(1)-O(2)	56.30(3)
C(1)-Ru(1)-O(1)	167.26(3)
C(1)-Ru(1)-O(2)	96.27(4)
C(1)-Ru(1)-O(3)	103.07(3)
C(1)-Ru(1)-C(5)	78.12(4)
C(5)-Ru(1)-O(1)	98.13(4)
C(5)-Ru(1)-O(2)	97.74(3)
C(5)-Ru(1)-O(3)	154.04(3)
C(26)-Ru(1)-O(1)	78.32(4)
C(26)-Ru(1)-O(2)	162.87(4)
C(26)-Ru(1)-O(3)	106.79(4)
C(26)-Ru(1)-C(1)	90.17(4)
C(26)-Ru(1)-C(5)	99.12(4)
C(32)-O(1)-Ru(1)	109.91(6)
C(32)-O(1)-C(33)	113.64(13)
C(32)-O(1)-C(33A)	130.6(2)
C(33)-O(1)-Ru(1)	135.68(11)
C(33A)-O(1)-Ru(1)	119.24(19)
N(3)-O(2)-Ru(1)	92.22(6)
N(3)-O(3)-Ru(1)	95.97(6)
C(1)-N(1)-C(2)	111.76(8)
C(1)-N(1)-C(4)	117.62(8)
C(4)-N(1)-C(2)	125.98(8)
C(1)-N(2)-C(3)	111.65(8)
C(1)-N(2)-C(14)	125.66(8)
C(14)-N(2)-C(3)	121.12(8)
O(3)-N(3)-O(2)	115.45(9)
O(4)-N(3)-O(2)	122.36(10)
O(4)-N(3)-O(3)	122.19(10)
N(1)-C(1)-Ru(1)	118.36(7)
N(2)-C(1)-Ru(1)	133.83(7)

N(2)-C(1)-N(1)	107.44(8)
N(1)-C(2)-C(3)	100.69(8)
N(1)-C(2)-H(2A)	110.4(8)
N(1)-C(2)-H(2B)	110.1(9)
C(3)-C(2)-H(2A)	113.8(8)
C(3)-C(2)-H(2B)	112.9(9)
H(2A)-C(2)-H(2B)	108.6(12)
N(2)-C(3)-C(2)	101.88(8)
N(2)-C(3)-H(3A)	109.7(9)
N(2)-C(3)-H(3B)	111.5(7)
C(2)-C(3)-H(3A)	113.4(9)
C(2)-C(3)-H(3B)	112.7(7)
H(3A)-C(3)-H(3B)	107.7(11)
N(1)-C(4)-C(5)	103.97(7)
N(1)-C(4)-C(11)	112.42(9)
N(1)-C(4)-C(12)	111.62(8)
C(5)-C(4)-C(11)	109.29(9)
C(12)-C(4)-C(5)	111.86(8)
C(12)-C(4)-C(11)	107.71(8)
Ru(1)-C(5)-H(5)	92.5(10)
C(4)-C(5)-Ru(1)	111.64(6)
C(4)-C(5)-H(5)	105.4(10)
C(6)-C(5)-Ru(1)	125.59(8)
C(6)-C(5)-C(4)	109.03(8)
C(6)-C(5)-H(5)	109.8(10)
C(5)-C(6)-C(13)	107.77(10)
C(5)-C(6)-H(6)	110.8(9)
C(7)-C(6)-C(5)	111.24(9)
C(7)-C(6)-C(13)	108.79(9)
C(7)-C(6)-H(6)	110.7(9)
C(13)-C(6)-H(6)	107.4(9)
C(6)-C(7)-C(8)	109.98(10)
C(6)-C(7)-H(7A)	108.8(9)
C(6)-C(7)-H(7B)	110.1(9)
C(8)-C(7)-H(7A)	107.8(9)
C(8)-C(7)-H(7B)	110.7(9)
H(7A)-C(7)-H(7B)	109.4(13)
C(7)-C(8)-C(9)	109.89(9)
C(7)-C(8)-C(12)	109.11(8)
C(7)-C(8)-H(8)	108.3(9)
C(9)-C(8)-C(12)	109.14(9)
C(9)-C(8)-H(8)	110.4(9)
C(12)-C(8)-H(8)	110.0(9)
C(8)-C(9)-H(9A)	110.3(9)
C(8)-C(9)-H(9B)	108.4(9)
C(10)-C(9)-C(8)	109.23(8)
C(10)-C(9)-H(9A)	110.8(9)
C(10)-C(9)-H(9B)	109.8(9)
H(9A)-C(9)-H(9B)	108.3(12)
C(9)-C(10)-C(11)	109.45(10)
C(9)-C(10)-C(13)	108.97(11)

C(9)-C(10)-H(10)	109.0(9)
C(11)-C(10)-H(10)	108.5(9)
C(13)-C(10)-C(11)	110.32(9)
C(13)-C(10)-H(10)	110.6(9)
C(4)-C(11)-C(10)	108.75(9)
C(4)-C(11)-H(11A)	107.5(9)
C(4)-C(11)-H(11B)	111.6(10)
C(10)-C(11)-H(11A)	113.5(9)
C(10)-C(11)-H(11B)	107.9(10)
H(11A)-C(11)-H(11B)	107.6(13)
C(4)-C(12)-C(8)	109.82(8)
C(4)-C(12)-H(12A)	109.0(10)
C(4)-C(12)-H(12B)	108.4(8)
C(8)-C(12)-H(12A)	111.0(9)
C(8)-C(12)-H(12B)	110.7(8)
H(12A)-C(12)-H(12B)	107.8(12)
C(6)-C(13)-H(13A)	109.9(9)
C(6)-C(13)-H(13B)	109.4(9)
C(10)-C(13)-C(6)	109.97(9)
C(10)-C(13)-H(13A)	110.6(8)
C(10)-C(13)-H(13B)	108.6(9)
H(13A)-C(13)-H(13B)	108.3(13)
C(15)-C(14)-N(2)	119.50(9)
C(19)-C(14)-N(2)	118.53(9)
C(19)-C(14)-C(15)	121.93(9)
C(14)-C(15)-C(20)	123.02(9)
C(16)-C(15)-C(14)	117.57(10)
C(16)-C(15)-C(20)	119.39(10)
C(15)-C(16)-H(16)	117.6(9)
C(17)-C(16)-C(15)	121.21(11)
C(17)-C(16)-H(16)	121.2(9)
C(16)-C(17)-H(17)	120.5(10)
C(18)-C(17)-C(16)	120.33(10)
C(18)-C(17)-H(17)	119.2(10)
C(17)-C(18)-C(19)	121.05(10)
C(17)-C(18)-H(18)	120.1(8)
C(19)-C(18)-H(18)	118.8(8)
C(14)-C(19)-C(23)	122.48(9)
C(18)-C(19)-C(14)	117.91(10)
C(18)-C(19)-C(23)	119.61(10)
C(15)-C(20)-C(21)	113.14(9)
C(15)-C(20)-C(22)	110.96(9)
C(15)-C(20)-H(20)	109.7(8)
C(21)-C(20)-H(20)	106.3(8)
C(22)-C(20)-C(21)	108.82(9)
C(22)-C(20)-H(20)	107.6(8)
C(20)-C(21)-H(21A)	114.2(10)
C(20)-C(21)-H(21B)	110.9(9)
C(20)-C(21)-H(21C)	112.1(11)
H(21A)-C(21)-H(21B)	108.3(13)
H(21A)-C(21)-H(21C)	103.5(14)

H(21B)-C(21)-H(21C)	107.3(13)
C(20)-C(22)-H(22A)	111.2(10)
C(20)-C(22)-H(22B)	106.9(9)
C(20)-C(22)-H(22C)	111.2(10)
H(22A)-C(22)-H(22B)	111.0(13)
H(22A)-C(22)-H(22C)	107.7(13)
H(22B)-C(22)-H(22C)	108.9(13)
C(19)-C(23)-C(24)	111.28(10)
C(19)-C(23)-C(25)	111.27(10)
C(19)-C(23)-H(23)	107.0(8)
C(24)-C(23)-H(23)	107.9(9)
C(25)-C(23)-C(24)	110.85(10)
C(25)-C(23)-H(23)	108.3(8)
C(23)-C(24)-H(24A)	106.0(10)
C(23)-C(24)-H(24B)	111.0(10)
C(23)-C(24)-H(24C)	109.5(9)
H(24A)-C(24)-H(24B)	108.5(14)
H(24A)-C(24)-H(24C)	112.2(14)
H(24B)-C(24)-H(24C)	109.5(13)
C(23)-C(25)-H(25A)	109.0(10)
C(23)-C(25)-H(25B)	112.8(11)
C(23)-C(25)-H(25C)	112.5(10)
H(25A)-C(25)-H(25B)	105.8(14)
H(25A)-C(25)-H(25C)	109.5(14)
H(25B)-C(25)-H(25C)	107.0(14)
Ru(1)-C(26)-H(26)	125.9(9)
C(27)-C(26)-Ru(1)	119.82(7)
C(27)-C(26)-H(26)	114.1(9)
C(28)-C(27)-C(26)	123.25(10)
C(28)-C(27)-C(32)	118.17(10)
C(32)-C(27)-C(26)	118.55(9)
C(27)-C(28)-H(28)	117.5(9)
C(29)-C(28)-C(27)	120.77(12)
C(29)-C(28)-H(28)	121.7(9)
C(28)-C(29)-H(29)	117.9(11)
C(30)-C(29)-C(28)	119.59(12)
C(30)-C(29)-H(29)	122.5(11)
C(29)-C(30)-C(31)	121.28(12)
C(29)-C(30)-H(30)	120.1(10)
C(31)-C(30)-H(30)	118.5(10)
C(30)-C(31)-H(31)	123.0(11)
C(32)-C(31)-C(30)	119.11(12)
C(32)-C(31)-H(31)	117.9(11)
O(1)-C(32)-C(27)	113.38(9)
O(1)-C(32)-C(31)	125.59(11)
C(31)-C(32)-C(27)	121.02(11)
O(1)-C(33)-C(34)	111.3(2)
O(1)-C(33)-C(35)	105.19(17)
O(1)-C(33)-H(33)	105.8(12)
C(34)-C(33)-H(33)	112.0(13)
C(35)-C(33)-C(34)	112.5(2)

C(35)-C(33)-H(33)	109.8(13)
O(1)-C(33A)-H(33A)	108.1
O(1)-C(33A)-C(34A)	104.9(5)
O(1)-C(33A)-C(35A)	111.1(4)
C(34A)-C(33A)-H(33A)	108.1
C(34A)-C(33A)-C(35A)	116.1(5)
C(35A)-C(33A)-H(33A)	108.1
C(33)-C(34)-H(34A)	111.3(16)
C(33)-C(34)-H(34B)	106(2)
C(33)-C(34)-H(34C)	111.1(15)
H(34A)-C(34)-H(34B)	104(3)
H(34A)-C(34)-H(34C)	111(2)
H(34B)-C(34)-H(34C)	114(3)
C(33A)-C(34A)-H(34D)	109.5
C(33A)-C(34A)-H(34E)	109.5
C(33A)-C(34A)-H(34F)	109.5
H(34D)-C(34A)-H(34E)	109.5
H(34D)-C(34A)-H(34F)	109.5
H(34E)-C(34A)-H(34F)	109.5
C(33)-C(35)-H(35A)	105.8(15)
C(33)-C(35)-H(35B)	109.0(15)
C(33)-C(35)-H(35C)	107.8(17)
H(35A)-C(35)-H(35B)	114(2)
H(35A)-C(35)-H(35C)	110(2)
H(35B)-C(35)-H(35C)	111(2)
C(33A)-C(35A)-H(35D)	109.5
C(33A)-C(35A)-H(35E)	109.5
C(33A)-C(35A)-H(35F)	109.5
H(35D)-C(35A)-H(35E)	109.5
H(35D)-C(35A)-H(35F)	109.5
H(35E)-C(35A)-H(35F)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x 10^4$) for 1.35. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	126(1)	99(1)	95(1)	-5(1)	21(1)	3(1)
O(1)	230(4)	182(3)	157(3)	51(3)	51(3)	56(3)
O(2)	217(4)	292(4)	154(3)	-27(3)	32(3)	-91(3)
O(3)	192(4)	196(4)	151(3)	-27(3)	29(3)	-17(3)
O(4)	306(5)	540(6)	111(3)	-66(4)	45(3)	-80(5)
N(1)	154(4)	130(3)	110(3)	-34(3)	6(3)	17(3)
N(2)	144(4)	113(3)	117(3)	-22(3)	-4(3)	14(3)
N(3)	180(4)	277(5)	123(4)	-21(3)	11(3)	-8(4)

C(1)	130(4)	112(4)	103(3)	-15(3)	31(3)	-16(3)
C(2)	192(5)	169(4)	116(4)	-12(3)	6(3)	35(4)
C(3)	181(5)	160(4)	134(4)	-16(3)	-9(3)	42(4)
C(4)	156(4)	122(4)	116(4)	-35(3)	31(3)	-7(3)
C(5)	210(5)	114(4)	112(4)	-20(3)	49(3)	-14(3)
C(6)	349(6)	112(4)	146(4)	-21(3)	39(4)	23(4)
C(7)	253(5)	185(5)	212(5)	-57(4)	32(4)	64(4)
C(8)	230(5)	171(4)	151(4)	-44(3)	82(4)	-1(4)
C(9)	301(6)	168(4)	148(4)	-66(3)	51(4)	-8(4)
C(10)	292(6)	175(5)	208(5)	-97(4)	81(4)	-87(4)
C(11)	190(5)	225(5)	190(5)	-92(4)	51(4)	-53(4)
C(12)	212(5)	146(4)	112(4)	-20(3)	51(3)	-7(4)
C(13)	472(8)	131(4)	198(5)	-48(4)	119(5)	-68(5)
C(14)	168(4)	101(4)	128(4)	-27(3)	-3(3)	19(3)
C(15)	181(4)	129(4)	137(4)	-15(3)	17(3)	22(3)
C(16)	274(6)	174(5)	139(4)	-32(3)	35(4)	20(4)
C(17)	301(6)	169(5)	156(4)	-58(3)	-2(4)	4(4)
C(18)	230(5)	138(4)	187(4)	-40(3)	-15(4)	-14(4)
C(19)	173(4)	114(4)	159(4)	-15(3)	-1(3)	5(3)
C(20)	188(5)	157(4)	164(4)	-24(3)	42(3)	8(4)
C(21)	241(6)	229(5)	223(5)	33(4)	65(4)	-3(4)
C(22)	206(5)	225(5)	223(5)	-14(4)	43(4)	28(4)
C(23)	187(5)	142(4)	215(5)	-28(4)	38(4)	-33(4)
C(24)	194(5)	229(6)	379(7)	-31(5)	42(5)	-32(4)
C(25)	342(7)	195(5)	276(6)	28(4)	75(5)	-8(5)
C(26)	161(4)	129(4)	135(4)	0(3)	28(3)	-9(3)
C(27)	147(4)	170(4)	147(4)	-32(3)	32(3)	-17(3)
C(28)	187(5)	246(5)	200(5)	-49(4)	68(4)	-56(4)
C(29)	194(5)	362(7)	318(6)	-127(5)	115(5)	-66(5)
C(30)	164(5)	410(8)	357(7)	-130(6)	33(5)	45(5)
C(31)	222(5)	290(6)	246(5)	-54(5)	-3(4)	90(5)
C(32)	169(4)	194(5)	154(4)	-35(3)	25(3)	26(4)
C(33)	218(10)	171(8)	153(7)	40(6)	27(8)	43(8)
C(33A)	190(20)	360(30)	430(30)	260(20)	140(20)	87(19)
C(34)	279(14)	427(15)	171(9)	-32(9)	-17(9)	-45(10)
C(34A)	610(50)	1130(80)	200(20)	150(40)	110(30)	600(50)
C(35)	353(11)	253(10)	220(9)	107(7)	-10(8)	-72(8)
C(35A)	240(20)	260(20)	980(40)	170(20)	-100(20)	17(16)

Table 5. Hydrogen coordinates (x 10^3) and isotropic displacement parameters ($Å^2$x 10^3) for 1.35.

	x	y	z	U_{iso}
H(33A)	141	38	500	38
H(34D)	403	74	555	96

H(34E)	312	37	613	96
H(34F)	283	114	580	96
H(35D)	229	-32	394	78
H(35E)	242	-63	488	78
H(35F)	363	-28	458	78
H(2A)	-314(1)	216(1)	150(1)	17(3)
H(2B)	-179(2)	249(1)	141(1)	23(4)
H(3A)	-237(1)	334(1)	228(1)	15(3)
H(3B)	-336(1)	288(1)	266(1)	13(3)
H(5)	-111(2)	77(1)	328(1)	31(4)
H(6)	56(1)	-6(1)	323(1)	21(4)
H(7A)	131(2)	-23(1)	190(1)	34(4)
H(7B)	170(2)	53(1)	226(1)	24(4)
H(8)	77(1)	59(1)	83(1)	20(4)
H(9A)	-57(2)	-38(1)	72(1)	30(4)
H(9B)	-137(2)	26(1)	36(1)	26(4)
H(10)	-251(2)	-30(1)	131(1)	27(4)
H(11A)	-281(2)	93(1)	122(1)	30(4)
H(11B)	-291(2)	64(1)	211(1)	29(4)
H(12A)	35(2)	156(1)	162(1)	26(4)
H(12B)	-83(1)	144(1)	92(1)	11(3)
H(13A)	-70(1)	-78(1)	223(1)	23(4)
H(13B)	-160(2)	-37(1)	277(1)	29(4)
H(16)	-225(2)	350(1)	566(1)	17(4)
H(17)	-55(2)	429(1)	587(1)	33(4)
H(18)	76(1)	440(1)	478(1)	20(4)
H(20)	-308(1)	229(1)	404(1)	16(3)
H(21A)	-247(2)	198(1)	550(1)	26(4)
H(21B)	-388(2)	189(1)	521(1)	19(3)
H(21C)	-332(2)	249(1)	575(1)	40(5)
H(22A)	-454(2)	335(1)	466(1)	31(4)
H(22B)	-509(2)	266(1)	416(1)	25(4)
H(22C)	-443(1)	323(1)	370(1)	26(4)
H(23)	42(1)	335(1)	290(1)	16(3)
H(24A)	236(2)	392(1)	410(1)	33(4)
H(24B)	263(2)	357(1)	327(1)	30(4)
H(24C)	218(2)	311(1)	400(1)	28(4)
H(25A)	-35(2)	447(1)	268(1)	27(4)
H(25B)	99(2)	443(1)	242(1)	44(5)
H(25C)	85(2)	476(1)	328(1)	37(5)
H(26)	135(1)	230(1)	263(1)	24(4)
H(28)	344(1)	220(1)	217(1)	23(4)
H(29)	549(2)	174(1)	232(1)	33(4)
H(30)	621(2)	94(1)	340(1)	33(4)
H(31)	474(2)	57(1)	428(1)	39(5)
H(33)	332(2)	18(1)	474(1)	15(5)
H(34A)	430(3)	112(1)	553(2)	36(7)
H(34B)	380(3)	63(2)	609(2)	56(9)
H(34C)	300(3)	129(1)	586(2)	29(6)
H(35A)	111(2)	57(1)	539(2)	29(6)
H(35B)	186(2)	-16(1)	561(2)	32(7)

H(35C)	112(3)	1(1)	467(2)	40(7)

Table 6. Torsion angles [°] for 1.35.

Ru(1)-O(1)-C(32)-C(27)	-0.08(10)
Ru(1)-O(1)-C(32)-C(31)	-179.45(9)
Ru(1)-O(1)-C(33)-C(34)	-92.5(2)
Ru(1)-O(1)-C(33)-C(35)	29.6(2)
Ru(1)-O(1)-C(33A)-C(34A)	-112.4(4)
Ru(1)-O(1)-C(33A)-C(35A)	121.3(3)
Ru(1)-O(2)-N(3)-O(3)	2.39(10)
Ru(1)-O(2)-N(3)-O(4)	-177.41(10)
Ru(1)-O(3)-N(3)-O(2)	-2.48(10)
Ru(1)-O(3)-N(3)-O(4)	177.31(10)
Ru(1)-C(5)-C(6)-C(7)	-80.00(11)
Ru(1)-C(5)-C(6)-C(13)	160.83(7)
Ru(1)-C(26)-C(27)-C(28)	176.61(8)
Ru(1)-C(26)-C(27)-C(32)	-1.56(13)
O(1)-Ru(1)-C(26)-C(27)	1.07(7)
O(2)-Ru(1)-C(26)-C(27)	74.21(16)
O(3)-Ru(1)-C(26)-C(27)	82.87(8)
N(1)-C(2)-C(3)-N(2)	23.33(10)
N(1)-C(4)-C(5)-Ru(1)	-33.59(9)
N(1)-C(4)-C(5)-C(6)	-176.63(9)
N(1)-C(4)-C(11)-C(10)	-174.75(9)
N(1)-C(4)-C(12)-C(8)	174.06(8)
N(2)-C(14)-C(15)-C(16)	-178.38(9)
N(2)-C(14)-C(15)-C(20)	-0.09(15)
N(2)-C(14)-C(19)-C(18)	178.47(9)
N(2)-C(14)-C(19)-C(23)	-1.46(15)
C(1)-Ru(1)-C(26)-C(27)	-173.41(8)
C(1)-N(1)-C(2)-C(3)	-24.91(11)
C(1)-N(1)-C(4)-C(5)	22.83(12)
C(1)-N(1)-C(4)-C(11)	140.92(9)
C(1)-N(1)-C(4)-C(12)	-97.92(10)
C(1)-N(2)-C(3)-C(2)	-16.76(11)
C(1)-N(2)-C(14)-C(15)	-87.28(13)
C(1)-N(2)-C(14)-C(19)	95.09(12)
C(2)-N(1)-C(1)-Ru(1)	-158.61(7)
C(2)-N(1)-C(1)-N(2)	15.44(11)
C(2)-N(1)-C(4)-C(5)	176.57(9)
C(2)-N(1)-C(4)-C(11)	-65.34(13)
C(2)-N(1)-C(4)-C(12)	55.82(13)
C(3)-N(2)-C(1)-Ru(1)	174.54(8)
C(3)-N(2)-C(1)-N(1)	1.80(11)
C(3)-N(2)-C(14)-C(15)	77.23(12)
C(3)-N(2)-C(14)-C(19)	-100.41(12)
C(4)-N(1)-C(1)-Ru(1)	-1.28(12)
C(4)-N(1)-C(1)-N(2)	172.77(8)
C(4)-N(1)-C(2)-C(3)	-179.95(9)
C(4)-C(5)-C(6)-C(7)	56.59(12)

C(4)-C(5)-C(6)-C(13)	-62.58(11)
C(5)-Ru(1)-C(26)-C(27)	-95.42(8)
C(5)-C(4)-C(11)-C(10)	-59.84(11)
C(5)-C(4)-C(12)-C(8)	58.03(11)
C(5)-C(6)-C(7)-C(8)	-59.68(12)
C(5)-C(6)-C(13)-C(10)	60.83(12)
C(6)-C(7)-C(8)-C(9)	-59.64(11)
C(6)-C(7)-C(8)-C(12)	59.99(12)
C(7)-C(6)-C(13)-C(10)	-59.89(12)
C(7)-C(8)-C(9)-C(10)	60.10(12)
C(7)-C(8)-C(12)-C(4)	-58.97(12)
C(8)-C(9)-C(10)-C(11)	60.18(13)
C(8)-C(9)-C(10)-C(13)	-60.54(12)
C(9)-C(8)-C(12)-C(4)	61.12(11)
C(9)-C(10)-C(11)-C(4)	-61.73(12)
C(9)-C(10)-C(13)-C(6)	60.91(12)
C(11)-C(4)-C(5)-Ru(1)	-153.81(7)
C(11)-C(4)-C(5)-C(6)	63.14(11)
C(11)-C(4)-C(12)-C(8)	-62.08(11)
C(11)-C(10)-C(13)-C(6)	-59.28(13)
C(12)-C(4)-C(5)-Ru(1)	87.00(8)
C(12)-C(4)-C(5)-C(6)	-56.04(11)
C(12)-C(4)-C(11)-C(10)	61.88(11)
C(12)-C(8)-C(9)-C(10)	-59.50(12)
C(13)-C(6)-C(7)-C(8)	58.88(12)
C(13)-C(10)-C(11)-C(4)	58.17(12)
C(14)-N(2)-C(1)-Ru(1)	-19.71(16)
C(14)-N(2)-C(1)-N(1)	167.56(9)
C(14)-N(2)-C(3)-C(2)	176.74(9)
C(14)-C(15)-C(16)-C(17)	-0.02(16)
C(14)-C(15)-C(20)-C(21)	133.53(11)
C(14)-C(15)-C(20)-C(22)	-103.83(11)
C(14)-C(19)-C(23)-C(24)	-120.52(11)
C(14)-C(19)-C(23)-C(25)	115.32(11)
C(15)-C(14)-C(19)-C(18)	0.89(15)
C(15)-C(14)-C(19)-C(23)	-179.03(10)
C(15)-C(16)-C(17)-C(18)	0.79(18)
C(16)-C(15)-C(20)-C(21)	-48.21(13)
C(16)-C(15)-C(20)-C(22)	74.43(12)
C(16)-C(17)-C(18)-C(19)	-0.72(18)
C(17)-C(18)-C(19)-C(14)	-0.11(16)
C(17)-C(18)-C(19)-C(23)	179.82(10)
C(18)-C(19)-C(23)-C(24)	59.56(13)
C(18)-C(19)-C(23)-C(25)	-64.61(14)
C(19)-C(14)-C(15)-C(16)	-0.83(15)
C(19)-C(14)-C(15)-C(20)	177.46(9)
C(20)-C(15)-C(16)-C(17)	-178.38(10)
C(26)-C(27)-C(28)-C(29)	-178.06(11)
C(26)-C(27)-C(32)-O(1)	0.94(13)
C(26)-C(27)-C(32)-C(31)	-179.67(10)
C(27)-C(28)-C(29)-C(30)	-1.88(18)

C(28)-C(27)-C(32)-O(1)	-177.33(9)
C(28)-C(27)-C(32)-C(31)	2.07(16)
C(28)-C(29)-C(30)-C(31)	1.5(2)
C(29)-C(30)-C(31)-C(32)	0.7(2)
C(30)-C(31)-C(32)-O(1)	176.85(11)
C(30)-C(31)-C(32)-C(27)	-2.47(18)
C(32)-O(1)-C(33)-C(34)	76.2(2)
C(32)-O(1)-C(33)-C(35)	-161.81(14)
C(32)-O(1)-C(33A)-C(34A)	74.3(5)
C(32)-O(1)-C(33A)-C(35A)	-51.9(5)
C(32)-C(27)-C(28)-C(29)	0.12(16)
C(33)-O(1)-C(32)-C(27)	-171.65(12)
C(33)-O(1)-C(32)-C(31)	8.99(17)
C(33)-O(1)-C(33A)-C(34A)	33.7(6)
C(33)-O(1)-C(33A)-C(35A)	-92.5(7)
C(33A)-O(1)-C(32)-C(27)	173.6(4)
C(33A)-O(1)-C(32)-C(31)	-5.7(4)
C(33A)-O(1)-C(33)-C(34)	-136.5(9)
C(33A)-O(1)-C(33)-C(35)	-14.5(7)

Symmetry transformations used to generate equivalent atoms:

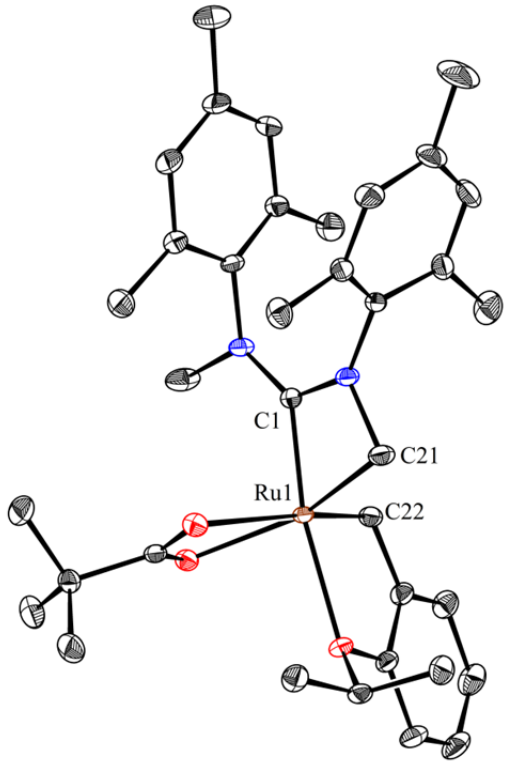


Table 1. Crystal Data and Structure Analysis Details for 1.41.

Empirical formula	C36 H48 N2 O3 Ru
Formula weight	657.83
Crystallization solvent	pentane/diethyl ether
Crystal shape	plate
Crystal color	dichroic purple blue
Crystal size	0.05 x 0.16 x 0.24 mm

Data Collection

Preliminary photograph(s)	rotation	
Type of diffractometer	Bruker APEX-II CCD	
Wavelength	0.71073 Å MoK	
Data collection temperature	100 K	
Theta range for 9892 reflections used in lattice determination	2.35 to 31.36°	
Unit cell dimensions	a = 7.6533(4) Å	□= 106.867(2)°
	b = 14.3189(7) Å	□= 101.578(2)°
	c = 16.6863(9) Å	□ = 100.570(2)°
Volume	1656.39(15) Å^3	

Z	2
Crystal system	triclinic
Space group	P -1 (# 2)
Density (calculated)	1.319 g/cm^3
F(000)	692
Theta range for data collection	1.5 to 37.1°
Completeness to theta = 25.000°	100.0%
Index ranges	-12 □ h □ 12, -23 □ k □ 23, -27 □ l □ 27
Data collection scan type	ω scans
Reflections collected	124448
Independent reflections	15920 [R_{int}= 0.0751]
Reflections > 2□(I)	12913
Average □(I)/(net I)	0.0504
Absorption coefficient	0.51 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.9066

Structure Solution and Refinement

Primary solution method	dual
Hydrogen placement	difmap
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15920 / 0 / 571
Treatment of hydrogen atoms	refall
Goodness-of-fit on F^2	1.17
Final R indices [I>2□(I), 12913 reflections]	R1 = 0.0355, wR2 = 0.0705
R indices (all data)	R1 = 0.0541, wR2 = 0.0754
Type of weighting scheme used	calc
Weighting scheme used	w=1/[^2^(Fo^2^)+(0.0300P)^2^] where P=(Fo^2^+2Fc^2^)/3
Max shift/error	0.001
Average shift/error	0.000
Extinction coefficient	n/a
Largest diff. peak and hole	0.99 and -0.85 e·Å^{-3}

Programs Used

Cell refinement	SAINT V8.32B (Bruker-AXS, 2007)

Data collection	APEX2 2013.6-2 (Bruker-AXS, 2007)
Data reduction	SAINT V8.32B (Bruker-AXS, 2007)
Structure solution	SHELXT (Sheldrick, 2012)
Structure refinement	SHELXL-2013/2 (Sheldrick, 2013)
Graphics	DIAMOND 3 (Crystal Impact, 1999)

Special Refinement Details

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 1.41. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Ru(1)	4268(1)	3169(1)	1755(1)	11(1)
O(1)	2918(1)	4144(1)	1067(1)	14(1)
O(2)	6487(1)	4560(1)	2460(1)	14(1)
O(3)	4545(1)	4145(1)	3181(1)	16(1)
N(1)	6757(1)	2051(1)	2557(1)	14(1)
N(2)	3484(1)	1471(1)	2026(1)	14(1)
C(1)	5099(2)	2139(1)	2180(1)	12(1)
C(2)	7050(2)	1312(1)	2969(1)	13(1)
C(3)	7156(2)	1568(1)	3858(1)	16(1)
C(4)	7371(2)	840(1)	4245(1)	21(1)
C(5)	7512(2)	-109(1)	3777(1)	23(1)
C(6)	7517(2)	-310(1)	2914(1)	20(1)
C(7)	7316(2)	395(1)	2496(1)	15(1)
C(8)	7090(2)	2604(1)	4389(1)	22(1)
C(9)	7639(3)	-903(2)	4198(1)	40(1)
C(10)	7449(2)	164(1)	1579(1)	22(1)
C(11)	8402(2)	2845(1)	2683(1)	25(1)
C(12)	2947(2)	517(1)	2144(1)	13(1)
C(13)	2568(2)	476(1)	2919(1)	16(1)
C(14)	2112(2)	-465(1)	3017(1)	22(1)
C(15)	1959(2)	-1353(1)	2357(1)	25(1)
C(16)	2179(2)	-1290(1)	1570(1)	24(1)
C(17)	2652(2)	-370(1)	1442(1)	18(1)
C(18)	2562(2)	1406(1)	3630(1)	23(1)
C(19)	1545(3)	-2363(1)	2488(2)	45(1)
C(20)	2758(2)	-340(1)	557(1)	27(1)
C(21)	2163(2)	1954(1)	1628(1)	17(1)
C(22)	4573(2)	2642(1)	659(1)	15(1)
C(23)	4074(2)	3133(1)	22(1)	16(1)
C(24)	4456(2)	2885(1)	-790(1)	20(1)
C(25)	3981(2)	3398(1)	-1356(1)	24(1)
C(26)	3106(2)	4163(1)	-1124(1)	24(1)

C(27)	2697(2)	4419(1)	-326(1)	19(1)
C(28)	3183(2)	3907(1)	240(1)	15(1)
C(29)	1207(2)	4436(1)	1173(1)	16(1)
C(30)	-426(2)	3542(1)	668(1)	23(1)
C(31)	1377(2)	4815(1)	2130(1)	21(1)
C(32)	5924(2)	4749(1)	3143(1)	13(1)
C(33)	6915(2)	5716(1)	3918(1)	16(1)
C(34)	8559(2)	6321(1)	3740(1)	24(1)
C(35)	5522(2)	6348(1)	4071(1)	26(1)
C(36)	7547(2)	5423(1)	4721(1)	25(1)

Table 3. Bond lengths [Å] and angles [°] for 1.41.

Ru(1)-O(1)	2.3063(9)
Ru(1)-O(2)	2.1975(9)
Ru(1)-O(3)	2.3278(9)
Ru(1)-C(1)	1.9631(12)
Ru(1)-C(21)	2.0716(13)
Ru(1)-C(22)	1.8451(13)
O(1)-C(28)	1.3879(15)
O(1)-C(29)	1.4732(15)
O(2)-C(32)	1.2715(15)
O(3)-C(32)	1.2609(15)
N(1)-C(1)	1.3439(16)
N(1)-C(2)	1.4453(15)
N(1)-C(11)	1.4669(18)
N(2)-C(1)	1.3440(15)
N(2)-C(12)	1.4328(15)
N(2)-C(21)	1.4819(16)
C(2)-C(3)	1.4024(18)
C(2)-C(7)	1.3969(17)
C(3)-C(4)	1.3939(18)
C(3)-C(8)	1.5060(19)
C(4)-H(4)	0.980(16)
C(4)-C(5)	1.392(2)
C(5)-C(6)	1.384(2)
C(5)-C(9)	1.508(2)
C(6)-H(6)	0.942(17)
C(6)-C(7)	1.3964(18)
C(7)-C(10)	1.499(2)
C(8)-H(8A)	0.99(2)
C(8)-H(8B)	0.94(2)
C(8)-H(8C)	0.980(19)
C(9)-H(9A)	0.92(3)
C(9)-H(9B)	0.94(3)
C(9)-H(9C)	0.85(3)
C(10)-H(10A)	0.91(2)
C(10)-H(10B)	0.85(2)
C(10)-H(10C)	0.95(2)
C(11)-H(11A)	0.92(2)
C(11)-H(11B)	0.89(3)

C(11)-H(11C)	0.95(4)
C(12)-C(13)	1.3964(17)
C(12)-C(17)	1.4008(17)
C(13)-C(14)	1.3946(18)
C(13)-C(18)	1.5048(19)
C(14)-H(14)	0.915(19)
C(14)-C(15)	1.386(2)
C(15)-C(16)	1.382(2)
C(15)-C(19)	1.511(2)
C(16)-H(16)	0.881(18)
C(16)-C(17)	1.391(2)
C(17)-C(20)	1.507(2)
C(18)-H(18A)	0.923(19)
C(18)-H(18B)	0.950(19)
C(18)-H(18C)	0.963(19)
C(19)-H(19A)	0.91(3)
C(19)-H(19B)	0.86(4)
C(19)-H(19C)	0.87(3)
C(20)-H(20A)	0.88(2)
C(20)-H(20B)	0.94(2)
C(20)-H(20C)	0.97(2)
C(21)-H(21A)	0.925(17)
C(21)-H(21B)	0.948(17)
C(22)-H(22)	1.007(18)
C(22)-C(23)	1.4623(17)
C(23)-C(24)	1.4021(18)
C(23)-C(28)	1.4038(18)
C(24)-H(24)	0.970(18)
C(24)-C(25)	1.388(2)
C(25)-H(25)	0.931(19)
C(25)-C(26)	1.387(2)
C(26)-H(26)	0.962(19)
C(26)-C(27)	1.388(2)
C(27)-H(27)	0.882(18)
C(27)-C(28)	1.3887(17)
C(29)-H(29)	0.969(16)
C(29)-C(30)	1.5078(19)
C(29)-C(31)	1.499(2)
C(30)-H(30A)	0.929(18)
C(30)-H(30B)	0.952(18)
C(30)-H(30C)	0.983(19)
C(31)-H(31A)	0.942(17)
C(31)-H(31B)	0.955(18)
C(31)-H(31C)	0.981(19)
C(32)-C(33)	1.5313(17)
C(33)-C(34)	1.523(2)
C(33)-C(35)	1.533(2)
C(33)-C(36)	1.532(2)
C(34)-H(34A)	0.961(19)
C(34)-H(34B)	0.99(2)
C(34)-H(34C)	0.936(19)

C(35)-H(35A)	0.970(19)
C(35)-H(35B)	0.98(2)
C(35)-H(35C)	0.976(18)
C(36)-H(36A)	0.981(19)
C(36)-H(36B)	0.96(2)
C(36)-H(36C)	0.90(2)

O(1)-Ru(1)-O(3)	97.98(3)
O(2)-Ru(1)-O(1)	85.06(3)
O(2)-Ru(1)-O(3)	57.91(3)
C(1)-Ru(1)-O(1)	170.01(4)
C(1)-Ru(1)-O(2)	104.66(4)
C(1)-Ru(1)-O(3)	89.35(4)
C(1)-Ru(1)-C(21)	65.55(5)
C(21)-Ru(1)-O(1)	106.39(4)
C(21)-Ru(1)-O(2)	155.74(5)
C(21)-Ru(1)-O(3)	98.73(5)
C(22)-Ru(1)-O(1)	79.62(4)
C(22)-Ru(1)-O(2)	107.62(5)
C(22)-Ru(1)-O(3)	165.53(5)
C(22)-Ru(1)-C(1)	94.94(5)
C(22)-Ru(1)-C(21)	95.62(6)
C(28)-O(1)-Ru(1)	108.05(7)
C(28)-O(1)-C(29)	117.19(9)
C(29)-O(1)-Ru(1)	124.99(7)
C(32)-O(2)-Ru(1)	93.83(7)
C(32)-O(3)-Ru(1)	88.15(7)
C(1)-N(1)-C(2)	125.11(10)
C(1)-N(1)-C(11)	118.40(10)
C(2)-N(1)-C(11)	115.84(10)
C(1)-N(2)-C(12)	135.05(11)
C(1)-N(2)-C(21)	101.24(9)
C(12)-N(2)-C(21)	123.69(10)
N(1)-C(1)-Ru(1)	133.99(9)
N(1)-C(1)-N(2)	124.70(11)
N(2)-C(1)-Ru(1)	101.29(8)
C(3)-C(2)-N(1)	118.13(11)
C(7)-C(2)-N(1)	120.12(11)
C(7)-C(2)-C(3)	121.66(11)
C(2)-C(3)-C(8)	121.46(12)
C(4)-C(3)-C(2)	117.85(12)
C(4)-C(3)-C(8)	120.66(12)
C(3)-C(4)-H(4)	118.1(10)
C(5)-C(4)-C(3)	121.79(13)
C(5)-C(4)-H(4)	120.1(10)
C(4)-C(5)-C(9)	120.71(15)
C(6)-C(5)-C(4)	118.55(12)
C(6)-C(5)-C(9)	120.74(15)
C(5)-C(6)-H(6)	119.4(10)
C(5)-C(6)-C(7)	121.97(13)
C(7)-C(6)-H(6)	118.6(10)

C(2)-C(7)-C(10)	122.31(12)
C(6)-C(7)-C(2)	117.86(12)
C(6)-C(7)-C(10)	119.80(12)
C(3)-C(8)-H(8A)	110.7(11)
C(3)-C(8)-H(8B)	111.0(13)
C(3)-C(8)-H(8C)	111.5(11)
H(8A)-C(8)-H(8B)	102.2(16)
H(8A)-C(8)-H(8C)	110.2(15)
H(8B)-C(8)-H(8C)	110.8(16)
C(5)-C(9)-H(9A)	111.9(16)
C(5)-C(9)-H(9B)	111.8(16)
C(5)-C(9)-H(9C)	115.1(17)
H(9A)-C(9)-H(9B)	110(2)
H(9A)-C(9)-H(9C)	111(2)
H(9B)-C(9)-H(9C)	96(2)
C(7)-C(10)-H(10A)	108.7(15)
C(7)-C(10)-H(10B)	114.5(16)
C(7)-C(10)-H(10C)	113.5(13)
H(10A)-C(10)-H(10B)	106(2)
H(10A)-C(10)-H(10C)	112(2)
H(10B)-C(10)-H(10C)	102.2(19)
N(1)-C(11)-H(11A)	108.6(13)
N(1)-C(11)-H(11B)	111.4(15)
N(1)-C(11)-H(11C)	116(2)
H(11A)-C(11)-H(11B)	113(2)
H(11A)-C(11)-H(11C)	105(2)
H(11B)-C(11)-H(11C)	102(2)
C(13)-C(12)-N(2)	120.32(11)
C(13)-C(12)-C(17)	120.72(11)
C(17)-C(12)-N(2)	118.72(11)
C(12)-C(13)-C(18)	122.18(12)
C(14)-C(13)-C(12)	118.34(12)
C(14)-C(13)-C(18)	119.44(12)
C(13)-C(14)-H(14)	119.2(12)
C(15)-C(14)-C(13)	121.86(13)
C(15)-C(14)-H(14)	118.8(12)
C(14)-C(15)-C(19)	121.08(17)
C(16)-C(15)-C(14)	118.13(12)
C(16)-C(15)-C(19)	120.79(16)
C(15)-C(16)-H(16)	121.3(12)
C(15)-C(16)-C(17)	122.25(13)
C(17)-C(16)-H(16)	116.4(12)
C(12)-C(17)-C(20)	121.42(12)
C(16)-C(17)-C(12)	118.17(13)
C(16)-C(17)-C(20)	120.36(13)
C(13)-C(18)-H(18A)	113.4(11)
C(13)-C(18)-H(18B)	112.4(11)
C(13)-C(18)-H(18C)	111.4(11)
H(18A)-C(18)-H(18B)	106.0(15)
H(18A)-C(18)-H(18C)	106.9(15)
H(18B)-C(18)-H(18C)	106.3(15)

C(15)-C(19)-H(19A)	111(2)
C(15)-C(19)-H(19B)	117(2)
C(15)-C(19)-H(19C)	108(2)
H(19A)-C(19)-H(19B)	88(3)
H(19A)-C(19)-H(19C)	103(3)
H(19B)-C(19)-H(19C)	126(3)
C(17)-C(20)-H(20A)	112.9(14)
C(17)-C(20)-H(20B)	110.1(13)
C(17)-C(20)-H(20C)	108.7(14)
H(20A)-C(20)-H(20B)	108.8(18)
H(20A)-C(20)-H(20C)	102.0(18)
H(20B)-C(20)-H(20C)	114.2(18)
Ru(1)-C(21)-H(21A)	113.3(11)
Ru(1)-C(21)-H(21B)	120.0(10)
N(2)-C(21)-Ru(1)	91.92(8)
N(2)-C(21)-H(21A)	111.9(10)
N(2)-C(21)-H(21B)	113.5(10)
H(21A)-C(21)-H(21B)	105.9(15)
Ru(1)-C(22)-H(22)	129.8(10)
C(23)-C(22)-Ru(1)	118.60(9)
C(23)-C(22)-H(22)	111.5(10)
C(24)-C(23)-C(22)	123.89(12)
C(24)-C(23)-C(28)	117.94(12)
C(28)-C(23)-C(22)	118.16(11)
C(23)-C(24)-H(24)	118.8(11)
C(25)-C(24)-C(23)	120.86(14)
C(25)-C(24)-H(24)	120.3(11)
C(24)-C(25)-H(25)	116.3(11)
C(26)-C(25)-C(24)	120.00(13)
C(26)-C(25)-H(25)	123.7(11)
C(25)-C(26)-H(26)	120.6(11)
C(25)-C(26)-C(27)	120.45(13)
C(27)-C(26)-H(26)	118.8(11)
C(26)-C(27)-H(27)	119.7(11)
C(26)-C(27)-C(28)	119.38(13)
C(28)-C(27)-H(27)	120.9(11)
O(1)-C(28)-C(23)	115.02(10)
O(1)-C(28)-C(27)	123.54(12)
C(27)-C(28)-C(23)	121.37(12)
O(1)-C(29)-H(29)	108.5(10)
O(1)-C(29)-C(30)	109.26(11)
O(1)-C(29)-C(31)	107.22(10)
C(30)-C(29)-H(29)	108.3(10)
C(31)-C(29)-H(29)	110.0(10)
C(31)-C(29)-C(30)	113.46(12)
C(29)-C(30)-H(30A)	109.8(11)
C(29)-C(30)-H(30B)	113.6(11)
C(29)-C(30)-H(30C)	109.1(11)
H(30A)-C(30)-H(30B)	105.4(15)
H(30A)-C(30)-H(30C)	109.2(15)
H(30B)-C(30)-H(30C)	109.7(15)

C(29)-C(31)-H(31A)	109.5(10)
C(29)-C(31)-H(31B)	108.6(11)
C(29)-C(31)-H(31C)	112.6(11)
H(31A)-C(31)-H(31B)	111.4(14)
H(31A)-C(31)-H(31C)	107.7(14)
H(31B)-C(31)-H(31C)	107.0(15)
O(2)-C(32)-C(33)	119.96(11)
O(3)-C(32)-O(2)	120.06(11)
O(3)-C(32)-C(33)	119.98(11)
C(32)-C(33)-C(35)	107.73(11)
C(32)-C(33)-C(36)	108.50(11)
C(34)-C(33)-C(32)	111.20(11)
C(34)-C(33)-C(35)	109.74(12)
C(34)-C(33)-C(36)	110.41(12)
C(36)-C(33)-C(35)	109.18(12)
C(33)-C(34)-H(34A)	112.1(11)
C(33)-C(34)-H(34B)	109.2(11)
C(33)-C(34)-H(34C)	112.0(11)
H(34A)-C(34)-H(34B)	111.7(16)
H(34A)-C(34)-H(34C)	104.9(16)
H(34B)-C(34)-H(34C)	106.8(16)
C(33)-C(35)-H(35A)	111.4(12)
C(33)-C(35)-H(35B)	110.4(11)
C(33)-C(35)-H(35C)	110.3(10)
H(35A)-C(35)-H(35B)	105.3(15)
H(35A)-C(35)-H(35C)	109.3(15)
H(35B)-C(35)-H(35C)	110.1(15)
C(33)-C(36)-H(36A)	109.4(11)
C(33)-C(36)-H(36B)	113.1(12)
C(33)-C(36)-H(36C)	111.0(13)
H(36A)-C(36)-H(36B)	103.6(16)
H(36A)-C(36)-H(36C)	112.4(16)
H(36B)-C(36)-H(36C)	107.2(17)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x 10^4$) for 1.41. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	132(1)	103(1)	108(1)	51(1)	35(1)	51(1)
O(1)	140(4)	162(4)	149(4)	78(3)	33(3)	71(3)
O(2)	183(4)	131(4)	125(4)	50(3)	55(3)	49(3)
O(3)	183(4)	158(4)	154(4)	62(3)	70(3)	50(3)
N(1)	136(5)	138(4)	186(5)	95(4)	49(4)	53(4)
N(2)	140(5)	131(4)	175(5)	87(4)	25(4)	36(4)

C(1)	144(5)	125(5)	99(5)	38(4)	48(4)	54(4)
C(2)	133(5)	137(5)	159(5)	85(4)	29(4)	52(4)
C(3)	157(6)	170(5)	162(6)	66(4)	40(4)	55(4)
C(4)	255(7)	237(6)	166(6)	112(5)	32(5)	61(5)
C(5)	259(7)	193(6)	254(7)	145(5)	10(6)	49(5)
C(6)	224(6)	130(5)	239(7)	69(5)	27(5)	71(5)
C(7)	152(5)	145(5)	171(6)	62(4)	36(4)	54(4)
C(8)	254(7)	204(6)	201(7)	31(5)	64(6)	84(5)
C(9)	567(13)	289(8)	379(10)	251(8)	19(9)	95(9)
C(10)	274(7)	222(6)	187(6)	57(5)	88(6)	85(6)
C(11)	131(6)	265(7)	440(9)	235(7)	76(6)	62(5)
C(12)	130(5)	114(5)	152(5)	56(4)	21(4)	31(4)
C(13)	169(6)	153(5)	146(5)	54(4)	43(4)	32(4)
C(14)	230(7)	220(6)	246(7)	150(5)	70(5)	26(5)
C(15)	205(7)	147(6)	394(9)	136(6)	47(6)	7(5)
C(16)	216(7)	122(5)	305(8)	-2(5)	18(6)	26(5)
C(17)	164(6)	163(5)	167(6)	22(4)	27(5)	39(4)
C(18)	272(7)	223(6)	159(6)	27(5)	76(5)	47(5)
C(19)	456(12)	198(7)	707(15)	257(9)	119(11)	3(8)
C(20)	321(8)	326(8)	156(6)	33(6)	69(6)	116(7)
C(21)	151(6)	165(5)	229(6)	102(5)	37(5)	61(4)
C(22)	183(6)	130(5)	143(5)	52(4)	46(4)	62(4)
C(23)	172(6)	174(5)	131(5)	70(4)	32(4)	44(4)
C(24)	234(7)	242(6)	139(6)	67(5)	53(5)	65(5)
C(25)	259(7)	334(8)	142(6)	117(6)	58(5)	50(6)
C(26)	214(7)	319(7)	203(6)	179(6)	9(5)	32(6)
C(27)	180(6)	230(6)	215(6)	140(5)	32(5)	71(5)
C(28)	145(5)	166(5)	141(5)	80(4)	17(4)	32(4)
C(29)	138(5)	154(5)	202(6)	74(5)	31(5)	73(4)
C(30)	157(6)	234(7)	256(7)	67(6)	12(5)	29(5)
C(31)	200(6)	236(6)	201(6)	45(5)	47(5)	111(5)
C(32)	166(5)	125(5)	128(5)	58(4)	38(4)	66(4)
C(33)	195(6)	143(5)	131(5)	30(4)	41(4)	45(4)
C(34)	271(7)	205(6)	192(7)	33(5)	57(6)	-23(6)
C(35)	291(8)	191(6)	247(7)	-9(5)	50(6)	103(6)
C(36)	294(8)	271(7)	166(6)	85(6)	5(6)	40(6)

Table 5. Hydrogen coordinates (x 10^3) and isotropic displacement parameters ($Å^2$x 10^3) for 1.41.

	x	y	z	U_{iso}
H(4)	738(2)	100(1)	486(1)	15(4)
H(6)	767(2)	-94(1)	260(1)	20(4)
H(8A)	832(3)	309(2)	457(1)	34(5)
H(8B)	688(3)	261(2)	493(1)	43(6)

H(8C)	616(3)	285(1)	407(1)	31(5)
H(9A)	843(4)	-64(2)	475(2)	69(8)
H(9B)	798(4)	-145(2)	385(2)	74(9)
H(9C)	661(4)	-125(2)	420(2)	64(8)
H(10A)	865(4)	21(2)	158(2)	62(7)
H(10B)	711(3)	57(2)	133(2)	54(7)
H(10C)	667(3)	-47(2)	119(2)	55(7)
H(11A)	815(3)	316(2)	228(1)	44(6)
H(11B)	939(3)	260(2)	266(2)	58(7)
H(11C)	881(5)	337(3)	323(2)	125(13)
H(14)	184(3)	-50(1)	352(1)	31(5)
H(16)	198(2)	-184(1)	112(1)	27(5)
H(18A)	292(2)	200(1)	352(1)	29(5)
H(18B)	337(2)	149(1)	417(1)	27(5)
H(18C)	135(3)	137(1)	372(1)	29(5)
H(19A)	105(4)	-232(2)	294(2)	99(12)
H(19B)	245(5)	-252(3)	277(2)	116(13)
H(19C)	64(5)	-278(3)	205(2)	97(11)
H(20A)	306(3)	-87(2)	25(1)	46(6)
H(20B)	363(3)	25(2)	61(1)	39(6)
H(20C)	153(3)	-41(2)	21(2)	54(7)
H(21A)	137(2)	213(1)	196(1)	21(4)
H(21B)	140(2)	153(1)	107(1)	18(4)
H(22)	513(2)	207(1)	42(1)	28(5)
H(24)	512(2)	237(1)	-94(1)	27(5)
H(25)	430(2)	321(1)	-188(1)	27(5)
H(26)	284(3)	455(1)	-150(1)	30(5)
H(27)	220(2)	493(1)	-17(1)	24(5)
H(29)	110(2)	497(1)	93(1)	18(4)
H(30A)	-27(2)	299(1)	83(1)	24(5)
H(30B)	-58(2)	333(1)	6(1)	25(5)
H(30C)	-155(3)	371(1)	80(1)	30(5)
H(31A)	152(2)	430(1)	236(1)	20(4)
H(31B)	30(2)	503(1)	221(1)	24(4)
H(31C)	244(3)	540(1)	245(1)	27(5)
H(34A)	821(3)	649(1)	323(1)	30(5)
H(34B)	951(3)	594(2)	370(1)	32(5)
H(34C)	912(3)	694(1)	419(1)	29(5)
H(35A)	441(3)	596(2)	414(1)	33(5)
H(35B)	510(3)	655(1)	356(1)	33(5)
H(35C)	607(2)	695(1)	459(1)	22(4)
H(36A)	817(2)	604(1)	522(1)	28(5)
H(36B)	847(3)	506(2)	468(1)	33(5)
H(36C)	660(3)	504(2)	481(1)	37(5)

Table 6. Torsion angles [°] for 1.41.

Ru(1)-O(1)-C(28)-C(23)	3.18(12)
Ru(1)-O(1)-C(28)-C(27)	-173.82(10)
Ru(1)-O(1)-C(29)-C(30)	-75.93(12)
Ru(1)-O(1)-C(29)-C(31)	47.42(13)
Ru(1)-O(2)-C(32)-O(3)	2.33(12)
Ru(1)-O(2)-C(32)-C(33)	-177.23(10)
Ru(1)-O(3)-C(32)-O(2)	-2.20(11)
Ru(1)-O(3)-C(32)-C(33)	177.36(10)
Ru(1)-C(22)-C(23)-C(24)	171.63(11)
Ru(1)-C(22)-C(23)-C(28)	-7.42(16)
O(1)-Ru(1)-C(22)-C(23)	6.70(9)
O(2)-Ru(1)-C(22)-C(23)	-74.67(10)
O(2)-C(32)-C(33)-C(34)	-1.61(17)
O(2)-C(32)-C(33)-C(35)	118.67(13)
O(2)-C(32)-C(33)-C(36)	-123.24(13)
O(3)-Ru(1)-C(22)-C(23)	-75.0(2)
O(3)-C(32)-C(33)-C(34)	178.82(12)
O(3)-C(32)-C(33)-C(35)	-60.89(15)
O(3)-C(32)-C(33)-C(36)	57.20(16)
N(1)-C(2)-C(3)-C(4)	177.71(12)
N(1)-C(2)-C(3)-C(8)	-3.88(18)
N(1)-C(2)-C(7)-C(6)	-177.38(11)
N(1)-C(2)-C(7)-C(10)	4.55(19)
N(2)-C(12)-C(13)-C(14)	-177.86(12)
N(2)-C(12)-C(13)-C(18)	4.70(19)
N(2)-C(12)-C(17)-C(16)	178.36(12)
N(2)-C(12)-C(17)-C(20)	-4.36(19)
C(1)-Ru(1)-C(22)-C(23)	178.24(10)
C(1)-N(1)-C(2)-C(3)	-89.73(15)
C(1)-N(1)-C(2)-C(7)	93.60(15)
C(1)-N(2)-C(12)-C(13)	90.40(18)
C(1)-N(2)-C(12)-C(17)	-95.19(17)
C(1)-N(2)-C(21)-Ru(1)	-0.68(9)
C(2)-N(1)-C(1)-Ru(1)	168.00(10)
C(2)-N(1)-C(1)-N(2)	-9.6(2)
C(2)-C(3)-C(4)-C(5)	1.1(2)
C(3)-C(2)-C(7)-C(6)	6.08(19)
C(3)-C(2)-C(7)-C(10)	-172.00(13)
C(3)-C(4)-C(5)-C(6)	2.8(2)
C(3)-C(4)-C(5)-C(9)	-176.62(16)
C(4)-C(5)-C(6)-C(7)	-2.4(2)
C(5)-C(6)-C(7)-C(2)	-1.9(2)
C(5)-C(6)-C(7)-C(10)	176.19(14)
C(7)-C(2)-C(3)-C(4)	-5.68(19)
C(7)-C(2)-C(3)-C(8)	172.73(12)
C(8)-C(3)-C(4)-C(5)	-177.31(14)
C(9)-C(5)-C(6)-C(7)	177.03(16)
C(11)-N(1)-C(1)-Ru(1)	-2.30(19)
C(11)-N(1)-C(1)-N(2)	-179.94(13)

C(11)-N(1)-C(2)-C(3)	80.79(16)
C(11)-N(1)-C(2)-C(7)	-95.88(15)
C(12)-N(2)-C(1)-Ru(1)	178.79(12)
C(12)-N(2)-C(1)-N(1)	-2.9(2)
C(12)-N(2)-C(21)-Ru(1)	-179.03(10)
C(12)-C(13)-C(14)-C(15)	-2.5(2)
C(13)-C(12)-C(17)-C(16)	-7.26(19)
C(13)-C(12)-C(17)-C(20)	170.02(13)
C(13)-C(14)-C(15)-C(16)	-3.3(2)
C(13)-C(14)-C(15)-C(19)	177.28(16)
C(14)-C(15)-C(16)-C(17)	3.9(2)
C(15)-C(16)-C(17)-C(12)	1.3(2)
C(15)-C(16)-C(17)-C(20)	-176.05(14)
C(17)-C(12)-C(13)-C(14)	7.85(19)
C(17)-C(12)-C(13)-C(18)	-169.59(13)
C(18)-C(13)-C(14)-C(15)	175.03(14)
C(19)-C(15)-C(16)-C(17)	-176.65(16)
C(21)-Ru(1)-C(22)-C(23)	112.38(10)
C(21)-N(2)-C(1)-Ru(1)	0.73(10)
C(21)-N(2)-C(1)-N(1)	179.00(12)
C(21)-N(2)-C(12)-C(13)	-91.88(15)
C(21)-N(2)-C(12)-C(17)	82.52(16)
C(22)-C(23)-C(24)-C(25)	-178.46(13)
C(22)-C(23)-C(28)-O(1)	1.78(17)
C(22)-C(23)-C(28)-C(27)	178.85(12)
C(23)-C(24)-C(25)-C(26)	-0.4(2)
C(24)-C(23)-C(28)-O(1)	-177.33(11)
C(24)-C(23)-C(28)-C(27)	-0.26(19)
C(24)-C(25)-C(26)-C(27)	-0.1(2)
C(25)-C(26)-C(27)-C(28)	0.4(2)
C(26)-C(27)-C(28)-O(1)	176.59(12)
C(26)-C(27)-C(28)-C(23)	-0.2(2)
C(28)-O(1)-C(29)-C(30)	65.76(14)
C(28)-O(1)-C(29)-C(31)	-170.89(10)
C(28)-C(23)-C(24)-C(25)	0.6(2)
C(29)-O(1)-C(28)-C(23)	-144.54(11)
C(29)-O(1)-C(28)-C(27)	38.46(16)

Symmetry transformations used to generate equivalent atoms:

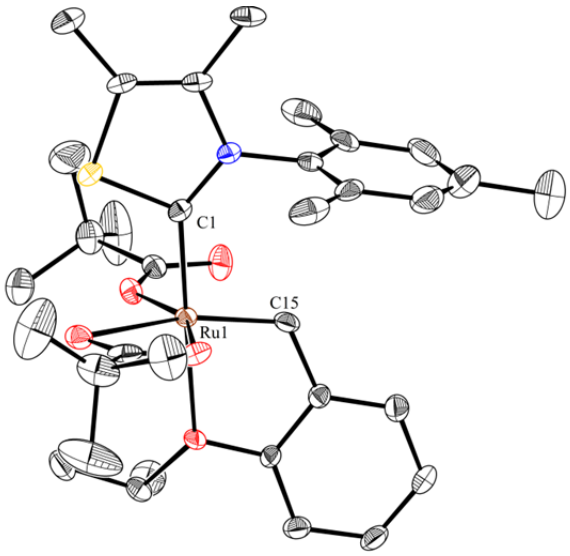


Table 1. Crystal Data and Structure Analysis Details for 1.43.

Empirical formula	C38 H57 N O6 Ru S	
Formula weight	756.97	
Crystallization solvent	pentane/ diethyl ether	
Crystal shape	tapered plate	
Crystal color	purple	
Crystal size	0.05 x 0.10 x 0.40 mm	

Data Collection

Preliminary photograph(s)	rotation	
Type of diffractometer	Bruker SMART 1000 ccd	
Wavelength	0.71073 Å MoK	
Data collection temperature	100 K	
Theta range for 9633 reflections used in lattice determination	2.22 to 29.09°	
Unit cell dimensions	a = 11.6331(10) Å b = 14.1980(13) Å c = 24.098(2) Å	a= 90° b= 90° g = 90°
Volume	3980.1(6) $Å^3$	
Z	4	
Crystal system	orthorhombic	
Space group	P 21 21 21 (# 19)	
Density (calculated)	1.263 g/cm^3	
F(000)	1600	

Theta range for data collection	1.7 to 32.8°
Completeness to theta = 25.000°	100.0%
Index ranges	-15 £ h £ 17, -21 £ k £ 18, -32 £ l £ 32
Data collection scan type	ω scans
Reflections collected	75804
Independent reflections	12393 [R_{int}= 0.0639]
Reflections > 2s(I)	10085
Average s(I)/(net I)	0.0709
Absorption coefficient	0.49 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.8912

Structure Solution and Refinement

Primary solution method	dual
Hydrogen placement	geom
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12393 / 0 / 470
Treatment of hydrogen atoms	constr
Goodness-of-fit on F^2	1.37
Final R indices [I>2s(I), 10085 reflections]	R1 = 0.0493, wR2 = 0.0700
R indices (all data)	R1 = 0.0727, wR2 = 0.0730
Type of weighting scheme used	calc
Weighting scheme used	w=1/[^2^(Fo^2^)+(0.0200P)^2^] where P=(Fo^2^+2Fc^2^)/3
Max shift/error	0.002
Average shift/error	0.000
Absolute structure parameter	-0.024(10)
Extinction coefficient	n/a
Largest diff. peak and hole	1.12 and -1.00 e·$Å^{-3}$

Programs Used

Cell refinement	SAINT V8.32B (Bruker-AXS, 2007)
Data collection	Bruker SMART v5.054 (Bruker-AXS, 2007)
Data reduction	SAINT V8.32B (Bruker-AXS, 2007)
Structure solution	SHELXT (Sheldrick, 2012)
Structure refinement	SHELXL-2013/2 (Sheldrick, 2013)

Special Refinement Details

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1.43. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Ru(1)	9036(1)	5229(1)	9342(1)	15(1)
S(1)	9385(1)	3099(1)	9662(1)	25(1)
O(1)	7992(2)	6595(1)	9364(1)	19(1)
O(2)	9083(2)	5248(2)	10174(1)	19(1)
O(3)	10616(2)	6117(2)	10401(1)	29(1)
O(4)	7443(2)	4231(2)	9256(1)	22(1)
O(5)	8345(2)	4898(2)	8559(1)	23(1)
N(1)	11049(2)	3822(2)	9172(1)	16(1)
C(1)	9983(3)	4079(2)	9346(2)	16(1)
C(2)	10593(3)	2397(2)	9560(2)	24(1)
C(3)	11391(3)	2880(2)	9286(2)	21(1)
C(4)	10625(3)	1392(3)	9751(2)	40(1)
C(5)	12547(3)	2535(2)	9085(2)	28(1)
C(6)	11820(3)	4458(2)	8885(2)	22(1)
C(7)	11702(3)	4563(2)	8310(2)	31(1)
C(8)	12435(4)	5200(3)	8050(2)	47(1)
C(9)	13245(4)	5696(3)	8338(2)	54(1)
C(10)	13356(3)	5569(3)	8905(2)	42(1)
C(11)	12639(3)	4922(2)	9194(2)	30(1)
C(12)	10810(4)	4038(3)	7993(2)	39(1)
C(13)	14025(5)	6414(4)	8040(3)	100(2)
C(14)	12723(3)	4815(3)	9808(2)	37(1)
C(15)	10118(3)	6085(2)	9105(1)	19(1)
C(16)	9743(3)	7041(2)	8971(1)	17(1)
C(17)	10442(3)	7690(2)	8700(1)	23(1)
C(18)	10044(3)	8601(2)	8597(2)	26(1)
C(19)	8957(3)	8855(2)	8770(1)	25(1)
C(20)	8239(3)	8221(2)	9035(1)	22(1)
C(21)	8638(3)	7306(2)	9122(1)	16(1)
C(22)	7009(3)	6876(2)	9707(2)	26(1)
C(23)	7528(4)	7387(3)	10222(2)	43(1)
C(24)	6381(3)	6024(3)	9890(2)	35(1)
C(25)	9815(3)	5597(2)	10523(1)	18(1)
C(26)	9640(3)	5244(3)	11124(1)	28(1)
C(27)	10244(4)	5890(4)	11532(2)	67(2)
C(28)	8368(3)	5170(3)	11266(2)	34(1)

C(29)	10165(4)	4247(3)	11151(2)	56(1)
C(30)	7568(3)	4343(2)	8739(2)	24(1)
C(31)	6823(3)	3815(3)	8325(2)	38(1)
C(32)	5816(8)	4498(7)	8201(5)	72(4)
C(33)	6523(11)	2910(7)	8497(4)	69(4)
C(34)	7468(8)	3789(7)	7730(3)	46(3)
C(32A)	5615(7)	3536(7)	8630(5)	52(4)
C(33A)	7453(9)	2809(6)	8288(5)	46(3)
C(34A)	6656(13)	4228(9)	7813(5)	72(5)
O(6)	1551(2)	1720(2)	7794(1)	36(1)
C(35)	-197(4)	1224(3)	8193(2)	62(2)
C(36)	421(4)	1423(3)	7669(2)	51(1)
C(37)	2192(4)	1976(3)	7315(2)	42(1)
C(38)	3321(4)	2378(4)	7499(2)	53(1)

Table 3. Bond lengths [Å] and angles [°] for 1.43.

Ru(1)-O(1)	2.2882(19)
Ru(1)-O(2)	2.0051(19)
Ru(1)-O(4)	2.342(2)
Ru(1)-O(5)	2.105(2)
Ru(1)-C(1)	1.970(3)
Ru(1)-C(15)	1.841(3)
Ru(1)-C(30)	2.571(3)
S(1)-C(1)	1.732(3)
S(1)-C(2)	1.740(3)
O(1)-C(21)	1.388(4)
O(1)-C(22)	1.466(4)
O(2)-C(25)	1.296(4)
O(3)-C(25)	1.225(4)
O(4)-C(30)	1.263(4)
O(5)-C(30)	1.276(4)
N(1)-C(1)	1.359(4)
N(1)-C(3)	1.423(4)
N(1)-C(6)	1.449(4)
C(2)-C(3)	1.330(5)
C(2)-C(4)	1.500(5)
C(3)-C(5)	1.511(4)
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-C(7)	1.400(5)
C(6)-C(11)	1.377(5)
C(7)-C(8)	1.391(5)
C(7)-C(12)	1.488(6)
C(8)-H(8)	0.9500
C(8)-C(9)	1.366(7)

C(9)-C(10)	1.384(7)
C(9)-C(13)	1.543(6)
C(10)-H(10)	0.9500
C(10)-C(11)	1.422(5)
C(11)-C(14)	1.491(5)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15)	0.9500
C(15)-C(16)	1.462(4)
C(16)-C(17)	1.391(5)
C(16)-C(21)	1.388(4)
C(17)-H(17)	0.9500
C(17)-C(18)	1.397(5)
C(18)-H(18)	0.9500
C(18)-C(19)	1.378(5)
C(19)-H(19)	0.9500
C(19)-C(20)	1.385(5)
C(20)-H(20)	0.9500
C(20)-C(21)	1.395(4)
C(22)-H(22)	1.0000
C(22)-C(23)	1.559(5)
C(22)-C(24)	1.480(5)
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-C(26)	1.546(5)
C(26)-C(27)	1.517(5)
C(26)-C(28)	1.522(5)
C(26)-C(29)	1.544(6)
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-C(31)	1.519(5)
C(31)-C(32)	1.550(9)
C(31)-C(33)	1.395(10)

C(31)-C(34)	1.619(9)
C(31)-C(32A)	1.635(11)
C(31)-C(33A)	1.607(10)
C(31)-C(34A)	1.381(11)
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800
C(32A)-H(32D)	0.9800
C(32A)-H(32E)	0.9800
C(32A)-H(32F)	0.9800
C(33A)-H(33D)	0.9800
C(33A)-H(33E)	0.9800
C(33A)-H(33F)	0.9800
C(34A)-H(34D)	0.9800
C(34A)-H(34E)	0.9800
C(34A)-H(34F)	0.9800
O(6)-C(36)	1.414(5)
O(6)-C(37)	1.421(5)
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
C(35)-C(36)	1.480(6)
C(36)-H(36A)	0.9900
C(36)-H(36B)	0.9900
C(37)-H(37A)	0.9900
C(37)-H(37B)	0.9900
C(37)-C(38)	1.499(6)
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800

O(1)-Ru(1)-O(4)	95.42(8)
O(1)-Ru(1)-C(30)	94.31(9)
O(2)-Ru(1)-O(1)	88.87(9)
O(2)-Ru(1)-O(4)	96.80(9)
O(2)-Ru(1)-O(5)	155.49(9)
O(2)-Ru(1)-C(30)	126.11(11)
O(4)-Ru(1)-C(30)	29.32(10)
O(5)-Ru(1)-O(1)	90.42(9)
O(5)-Ru(1)-O(4)	58.88(9)
O(5)-Ru(1)-C(30)	29.59(10)
C(1)-Ru(1)-O(1)	177.49(12)
C(1)-Ru(1)-O(2)	89.47(12)
C(1)-Ru(1)-O(4)	86.64(10)
C(1)-Ru(1)-O(5)	91.87(12)

C(1)-Ru(1)-C(30)	88.19(12)
C(15)-Ru(1)-O(1)	79.09(11)
C(15)-Ru(1)-O(2)	106.41(12)
C(15)-Ru(1)-O(4)	155.94(12)
C(15)-Ru(1)-O(5)	97.49(12)
C(15)-Ru(1)-C(1)	99.59(14)
C(15)-Ru(1)-C(30)	127.04(14)
C(1)-S(1)-C(2)	94.24(15)
C(21)-O(1)-Ru(1)	108.63(17)
C(21)-O(1)-C(22)	117.5(2)
C(22)-O(1)-Ru(1)	131.13(19)
C(25)-O(2)-Ru(1)	132.2(2)
C(30)-O(4)-Ru(1)	85.44(19)
C(30)-O(5)-Ru(1)	95.9(2)
C(1)-N(1)-C(3)	116.6(3)
C(1)-N(1)-C(6)	123.0(2)
C(3)-N(1)-C(6)	120.3(3)
S(1)-C(1)-Ru(1)	116.34(16)
N(1)-C(1)-Ru(1)	137.0(2)
N(1)-C(1)-S(1)	106.6(2)
C(3)-C(2)-S(1)	109.8(2)
C(3)-C(2)-C(4)	128.7(3)
C(4)-C(2)-S(1)	121.4(3)
N(1)-C(3)-C(5)	119.5(3)
C(2)-C(3)-N(1)	112.6(3)
C(2)-C(3)-C(5)	127.9(3)
C(2)-C(4)-H(4A)	109.5
C(2)-C(4)-H(4B)	109.5
C(2)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
C(3)-C(5)-H(5A)	109.5
C(3)-C(5)-H(5B)	109.5
C(3)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(7)-C(6)-N(1)	118.6(3)
C(11)-C(6)-N(1)	117.9(3)
C(11)-C(6)-C(7)	123.5(3)
C(6)-C(7)-C(12)	121.4(3)
C(8)-C(7)-C(6)	117.1(4)
C(8)-C(7)-C(12)	121.5(4)
C(7)-C(8)-H(8)	119.0
C(9)-C(8)-C(7)	121.9(4)
C(9)-C(8)-H(8)	119.0
C(8)-C(9)-C(10)	119.9(4)
C(8)-C(9)-C(13)	120.7(5)
C(10)-C(9)-C(13)	119.4(5)
C(9)-C(10)-H(10)	119.6

C(9)-C(10)-C(11)	120.8(4)
C(11)-C(10)-H(10)	119.6
C(6)-C(11)-C(10)	116.8(4)
C(6)-C(11)-C(14)	122.2(3)
C(10)-C(11)-C(14)	120.9(4)
C(7)-C(12)-H(12A)	109.5
C(7)-C(12)-H(12B)	109.5
C(7)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(9)-C(13)-H(13A)	109.5
C(9)-C(13)-H(13B)	109.5
C(9)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(11)-C(14)-H(14A)	109.5
C(11)-C(14)-H(14B)	109.5
C(11)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
Ru(1)-C(15)-H(15)	120.7
C(16)-C(15)-Ru(1)	118.5(2)
C(16)-C(15)-H(15)	120.7
C(17)-C(16)-C(15)	123.0(3)
C(21)-C(16)-C(15)	118.1(3)
C(21)-C(16)-C(17)	119.0(3)
C(16)-C(17)-H(17)	119.9
C(16)-C(17)-C(18)	120.2(3)
C(18)-C(17)-H(17)	119.9
C(17)-C(18)-H(18)	120.3
C(19)-C(18)-C(17)	119.5(3)
C(19)-C(18)-H(18)	120.3
C(18)-C(19)-H(19)	119.2
C(18)-C(19)-C(20)	121.5(3)
C(20)-C(19)-H(19)	119.2
C(19)-C(20)-H(20)	120.9
C(19)-C(20)-C(21)	118.2(3)
C(21)-C(20)-H(20)	120.9
O(1)-C(21)-C(20)	124.1(3)
C(16)-C(21)-O(1)	114.5(3)
C(16)-C(21)-C(20)	121.5(3)
O(1)-C(22)-H(22)	110.7
O(1)-C(22)-C(23)	105.9(3)
O(1)-C(22)-C(24)	109.3(3)
C(23)-C(22)-H(22)	110.7
C(24)-C(22)-H(22)	110.7
C(24)-C(22)-C(23)	109.5(3)
C(22)-C(23)-H(23A)	109.5

C(22)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
O(2)-C(25)-C(26)	113.4(3)
O(3)-C(25)-O(2)	125.1(3)
O(3)-C(25)-C(26)	121.4(3)
C(27)-C(26)-C(25)	110.5(3)
C(27)-C(26)-C(28)	110.2(4)
C(27)-C(26)-C(29)	110.1(4)
C(28)-C(26)-C(25)	111.2(3)
C(28)-C(26)-C(29)	108.2(4)
C(29)-C(26)-C(25)	106.5(3)
C(26)-C(27)-H(27A)	109.5
C(26)-C(27)-H(27B)	109.5
C(26)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(26)-C(28)-H(28A)	109.5
C(26)-C(28)-H(28B)	109.5
C(26)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(26)-C(29)-H(29A)	109.5
C(26)-C(29)-H(29B)	109.5
C(26)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
O(4)-C(30)-Ru(1)	65.24(17)
O(4)-C(30)-O(5)	119.7(3)
O(4)-C(30)-C(31)	121.3(3)
O(5)-C(30)-Ru(1)	54.52(16)
O(5)-C(30)-C(31)	119.0(3)
C(31)-C(30)-Ru(1)	172.5(3)
C(30)-C(31)-C(32)	104.4(4)
C(30)-C(31)-C(34)	109.2(4)
C(30)-C(31)-C(32A)	108.4(5)
C(30)-C(31)-C(33A)	102.4(4)
C(32)-C(31)-C(34)	101.1(7)
C(33)-C(31)-C(30)	113.7(5)
C(33)-C(31)-C(32)	116.4(7)

C(33)-C(31)-C(34)	111.0(6)
C(33A)-C(31)-C(32A)	101.6(6)
C(34A)-C(31)-C(30)	117.2(6)
C(34A)-C(31)-C(32A)	112.6(8)
C(34A)-C(31)-C(33A)	113.1(8)
C(31)-C(32)-H(32A)	109.5
C(31)-C(32)-H(32B)	109.5
C(31)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(31)-C(33)-H(33A)	109.5
C(31)-C(33)-H(33B)	109.5
C(31)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
C(31)-C(34)-H(34A)	109.5
C(31)-C(34)-H(34B)	109.5
C(31)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5
C(31)-C(32A)-H(32D)	109.5
C(31)-C(32A)-H(32E)	109.5
C(31)-C(32A)-H(32F)	109.5
H(32D)-C(32A)-H(32E)	109.5
H(32D)-C(32A)-H(32F)	109.5
H(32E)-C(32A)-H(32F)	109.5
C(31)-C(33A)-H(33D)	109.5
C(31)-C(33A)-H(33E)	109.5
C(31)-C(33A)-H(33F)	109.5
H(33D)-C(33A)-H(33E)	109.5
H(33D)-C(33A)-H(33F)	109.5
H(33E)-C(33A)-H(33F)	109.5
C(31)-C(34A)-H(34D)	109.5
C(31)-C(34A)-H(34E)	109.5
C(31)-C(34A)-H(34F)	109.5
H(34D)-C(34A)-H(34E)	109.5
H(34D)-C(34A)-H(34F)	109.5
H(34E)-C(34A)-H(34F)	109.5
C(36)-O(6)-C(37)	113.0(3)
H(35A)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(36)-C(35)-H(35A)	109.5
C(36)-C(35)-H(35B)	109.5
C(36)-C(35)-H(35C)	109.5
O(6)-C(36)-C(35)	109.1(4)
O(6)-C(36)-H(36A)	109.9
O(6)-C(36)-H(36B)	109.9

C(35)-C(36)-H(36A)	109.9
C(35)-C(36)-H(36B)	109.9
H(36A)-C(36)-H(36B)	108.3
O(6)-C(37)-H(37A)	110.0
O(6)-C(37)-H(37B)	110.0
O(6)-C(37)-C(38)	108.4(3)
H(37A)-C(37)-H(37B)	108.4
C(38)-C(37)-H(37A)	110.0
C(38)-C(37)-H(37B)	110.0
C(37)-C(38)-H(38A)	109.5
C(37)-C(38)-H(38B)	109.5
C(37)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x 10^4$) for 1.43. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	140(1)	112(1)	186(1)	-14(1)	6(1)	9(1)
S(1)	248(5)	170(4)	323(5)	88(4)	31(4)	24(3)
O(1)	146(10)	135(10)	286(13)	8(11)	55(11)	33(8)
O(2)	155(10)	200(10)	205(11)	-32(10)	16(10)	-29(13)
O(3)	267(14)	288(13)	316(15)	-2(11)	-11(11)	-151(11)
O(4)	175(11)	188(11)	311(16)	-12(11)	-43(11)	-6(9)
O(5)	300(13)	164(12)	221(13)	4(10)	-63(10)	40(10)
N(1)	191(14)	138(12)	166(14)	2(10)	-5(12)	22(12)
C(1)	219(16)	149(14)	99(15)	-4(15)	-1(16)	17(12)
C(2)	269(19)	167(16)	270(20)	43(15)	-36(15)	71(14)
C(3)	242(16)	168(15)	207(19)	-14(15)	-39(16)	80(13)
C(4)	390(20)	248(19)	560(30)	160(20)	-10(20)	65(17)
C(5)	300(20)	229(18)	300(20)	-41(16)	-26(17)	142(16)
C(6)	204(18)	132(15)	330(20)	-3(15)	98(15)	94(13)
C(7)	370(20)	240(20)	320(20)	103(16)	169(18)	184(16)
C(8)	510(30)	470(30)	440(30)	240(30)	220(20)	250(30)
C(9)	510(30)	390(30)	740(40)	250(30)	190(30)	100(20)
C(10)	180(20)	310(20)	780(40)	-10(20)	80(20)	46(16)
C(11)	171(17)	217(18)	510(30)	5(17)	78(16)	86(14)
C(12)	590(30)	370(20)	210(20)	28(17)	50(20)	230(20)
C(13)	710(40)	860(40)	1440(60)	610(40)	380(50)	-40(40)
C(14)	255(19)	291(19)	570(30)	-150(20)	-89(18)	54(18)
C(15)	145(16)	174(16)	260(19)	-15(15)	10(14)	44(13)
C(16)	179(17)	142(16)	194(19)	-7(14)	2(14)	-21(13)
C(17)	232(18)	216(17)	250(20)	12(15)	48(15)	-4(15)

C(18)	310(20)	190(17)	260(20)	78(16)	15(17)	-28(15)
C(19)	330(20)	153(15)	278(19)	62(14)	21(18)	34(16)
C(20)	223(18)	181(17)	260(20)	8(15)	-10(15)	41(14)
C(21)	173(16)	123(15)	182(18)	9(13)	15(13)	-7(12)
C(22)	225(18)	244(18)	310(20)	10(17)	139(16)	87(15)
C(23)	510(30)	330(20)	440(30)	-50(20)	110(20)	50(20)
C(24)	217(19)	280(20)	560(30)	14(19)	145(18)	10(15)
C(25)	169(16)	142(14)	240(20)	-49(14)	25(14)	6(13)
C(26)	320(20)	337(19)	173(18)	-40(19)	32(15)	-40(20)
C(27)	710(40)	1040(40)	240(30)	-100(30)	20(20)	-520(30)
C(28)	380(20)	380(20)	270(20)	20(20)	49(17)	-60(20)
C(29)	570(30)	690(30)	410(30)	250(30)	30(20)	210(30)
C(30)	251(19)	140(16)	310(20)	-59(16)	-104(16)	89(14)
C(31)	320(20)	380(20)	440(30)	-190(20)	-170(20)	6(18)
C(32)	390(60)	940(80)	840(80)	-430(60)	-450(50)	230(50)
C(33)	1080(110)	590(70)	400(60)	-70(50)	-160(60)	-460(70)
C(34)	480(60)	670(70)	250(50)	-100(40)	-100(40)	-140(50)
C(32A)	160(50)	450(60)	960(90)	-320(60)	-190(50)	-10(40)
C(33A)	380(60)	350(50)	640(80)	-290(50)	-100(60)	-50(40)
C(34A)	860(120)	670(90)	620(90)	190(70)	-510(90)	-190(80)
O(6)	507(18)	272(15)	289(16)	-7(12)	2(14)	5(13)
C(35)	660(30)	550(30)	640(40)	30(30)	-50(30)	-310(30)
C(36)	650(30)	390(30)	480(30)	-110(20)	-70(30)	-160(20)
C(37)	700(30)	340(20)	220(20)	-43(19)	60(20)	140(20)
C(38)	500(30)	740(40)	360(30)	110(30)	200(20)	210(30)

Table 5. Hydrogen coordinates (x 10^3) and isotropic displacement parameters (Å^{2}x 10^3) for 1.43.

	x	y	z	U_{iso}
H(4A)	1141	123	986	60
H(4B)	1038	98	945	60
H(4C)	1010	131	1007	60
H(5A)	1253	246	868	42
H(5B)	1272	192	926	42
H(5C)	1314	299	919	42
H(8)	1237	529	766	57
H(10)	1392	592	910	51
H(12A)	1094	412	760	58
H(12B)	1005	428	809	58
H(12C)	1086	337	809	58
H(13A)	1355	691	787	150
H(13B)	1446	609	775	150
H(13C)	1456	670	831	150
H(14A)	1274	414	990	56
H(14B)	1206	511	998	56
H(14C)	1343	512	994	56

H(15)	1090	591	907	23
H(17)	1119	751	859	28
H(18)	1052	904	841	31
H(19)	870	948	871	30
H(20)	749	840	915	26
H(22)	649	731	950	31
H(23A)	802	790	1010	64
H(23B)	798	694	1044	64
H(23C)	690	764	1045	64
H(24A)	691	560	1009	53
H(24B)	607	570	956	53
H(24C)	575	621	1014	53
H(27A)	1011	566	1191	100
H(27B)	994	653	1149	100
H(27C)	1107	589	1145	100
H(28A)	802	580	1126	51
H(28B)	828	490	1164	51
H(28C)	798	476	1099	51
H(29A)	1002	397	1152	84
H(29B)	1100	428	1108	84
H(29C)	981	385	1087	84
H(32A)	529	421	793	109
H(32B)	612	509	805	109
H(32C)	540	463	854	109
H(33A)	595	265	824	104
H(33B)	620	294	887	104
H(33C)	721	251	850	104
H(34A)	698	346	746	70
H(34B)	820	346	777	70
H(34C)	761	444	760	70
H(32D)	516	314	838	79
H(32E)	518	411	872	79
H(32F)	578	319	897	79
H(33D)	703	240	803	69
H(33E)	747	252	866	69
H(33F)	824	290	816	69
H(34D)	623	380	757	107
H(34E)	740	437	764	107
H(34F)	622	481	786	107
H(35A)	-25	180	841	92
H(35B)	22	74	840	92
H(35C)	-97	100	811	92
H(36A)	45	85	744	61
H(36B)	1	192	746	61
H(37A)	176	245	710	51
H(37B)	232	142	708	51
H(38A)	374	191	772	79
H(38B)	318	294	772	79
H(38C)	378	255	717	79

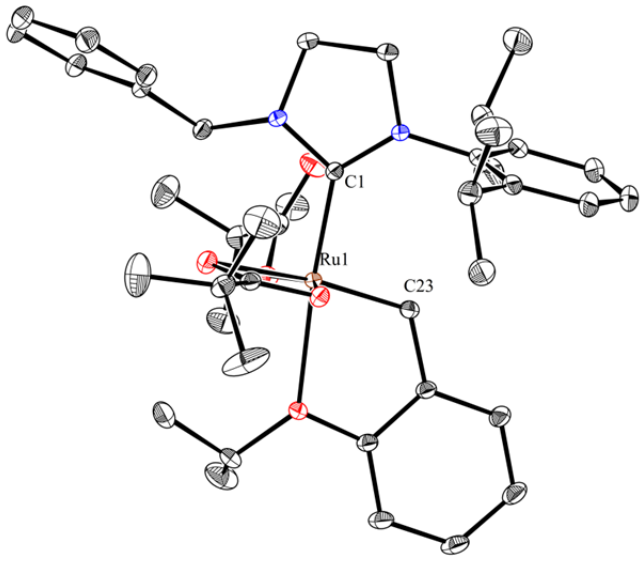


Table 1. Crystal Data and Structure Analysis Details for 1.45.

Empirical formula	C42 H58 N2 O5 Ru	
Formula weight	771.97	
Crystallization solvent	pentane/ diethyl ether	
Crystal shape	plate	
Crystal color	dichroic blue purple	
Crystal size	0.12 x 0.33 x 0.51 mm	

Data Collection

Preliminary photograph(s)	rotation	
Type of diffractometer	Bruker APEX-II CCD	
Wavelength	0.71073 Å MoK	
Data collection temperature	100 K	
Theta range for 9952 reflections used in lattice determination	2.35 to 38.07°	
Unit cell dimensions	a = 13.5593(4) Å b = 13.6048(4) Å c = 21.4584(7) Å	a= 90° b= 93.7230(17)° g = 90°
Volume	3950.1(2) $Å^3$	
Z	4	
Crystal system	monoclinic	
Space group	P 1 21/c 1 (# 14)	
Density (calculated)	1.298 g/cm^3	
F(000)	1632	

Theta range for data collection	1.5 to 42.2°
Completeness to theta = 25.000°	100.0%
Index ranges	-25 £ h £ 25, -25 £ k £ 25, -39 £ l £ 40
Data collection scan type	ω scans
Reflections collected	291197
Independent reflections	27418 [R_{int}= 0.0614]
Reflections > 2s(I)	21877
Average s(I)/(net I)	0.0346
Absorption coefficient	0.44 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.9046

Structure Solution and Refinement

Primary solution method	dual
Hydrogen placement	difmap
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	27418 / 0 / 683
Treatment of hydrogen atoms	refall
Goodness-of-fit on F^2	1.34
Final R indices [I>2s(I), 21877 reflections]	R1 = 0.0325, wR2 = 0.0743
R indices (all data)	R1 = 0.0489, wR2 = 0.0787
Type of weighting scheme used	calc
Weighting scheme used	w=1/[^2^(Fo^2^)+(0.0300P)^2^] where P=(Fo^2^+2Fc^2^)/3
Max shift/error	0.002
Average shift/error	0.000
Extinction coefficient	n/a
Largest diff. peak and hole	1.54 and -0.59 e·$Å^{-3}$

Programs Used

Cell refinement	SAINT V8.32B (Bruker-AXS, 2007)
Data collection	APEX2 2013.6-2 (Bruker-AXS, 2007)
Data reduction	SAINT V8.32B (Bruker-AXS, 2007)
Structure solution	SHELXT (Sheldrick, 2012)
Structure refinement	SHELXL-2013/2 (Sheldrick, 2013)
Graphics	DIAMOND 3 (Crystal Impact, 1999)

Special Refinement Details

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1.45. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Ru(1)	2644(1)	1846(1)	9403(1)	9(1)
O(1)	2149(1)	721(1)	10138(1)	14(1)
O(2)	2245(1)	787(1)	8715(1)	12(1)
O(3)	3829(1)	794(1)	8988(1)	15(1)
O(4)	3421(1)	2476(1)	10140(1)	14(1)
O(5)	3542(1)	4017(1)	9776(1)	19(1)
N(1)	3897(1)	2946(1)	8584(1)	12(1)
N(2)	2368(1)	3432(1)	8406(1)	12(1)
C(1)	2956(1)	2829(1)	8774(1)	10(1)
C(2)	3964(1)	3826(1)	8192(1)	17(1)
C(3)	2913(1)	3917(1)	7921(1)	17(1)
C(4)	4784(1)	2718(1)	8977(1)	13(1)
C(5)	5637(1)	2397(1)	8607(1)	13(1)
C(6)	5494(1)	1912(1)	8037(1)	17(1)
C(7)	6298(1)	1600(1)	7718(1)	21(1)
C(8)	7254(1)	1757(1)	7969(1)	23(1)
C(9)	7406(1)	2234(1)	8538(1)	22(1)
C(10)	6602(1)	2560(1)	8853(1)	18(1)
C(11)	1331(1)	3643(1)	8405(1)	13(1)
C(12)	1040(1)	4486(1)	8729(1)	16(1)
C(13)	32(1)	4706(1)	8711(1)	22(1)
C(14)	-656(1)	4129(1)	8376(1)	26(1)
C(15)	-349(1)	3324(1)	8044(1)	23(1)
C(16)	647(1)	3056(1)	8053(1)	17(1)
C(17)	1765(1)	5142(1)	9098(1)	19(1)
C(18)	1517(1)	5215(1)	9786(1)	29(1)
C(19)	1802(1)	6168(1)	8810(1)	28(1)
C(20)	952(1)	2163(1)	7691(1)	19(1)
C(21)	325(1)	1263(1)	7837(1)	25(1)
C(22)	888(1)	2367(1)	6987(1)	33(1)
C(23)	1410(1)	2317(1)	9552(1)	12(1)
C(24)	799(1)	1771(1)	9963(1)	12(1)
C(25)	-182(1)	2036(1)	10050(1)	16(1)
C(26)	-752(1)	1493(1)	10438(1)	20(1)
C(27)	-341(1)	676(1)	10747(1)	20(1)
C(28)	633(1)	396(1)	10673(1)	17(1)
C(29)	1194(1)	940(1)	10276(1)	12(1)
C(30)	2712(1)	43(1)	10560(1)	19(1)
C(31)	2888(1)	511(1)	11199(1)	30(1)
C(32)	3663(1)	-180(1)	10268(1)	37(1)
C(33)	3113(1)	435(1)	8666(1)	13(1)
C(34)	3246(1)	-408(1)	8211(1)	17(1)

C(35)	3046(1)	-6(1)	7548(1)	33(1)
C(36)	2508(1)	-1220(1)	8323(1)	43(1)
C(37)	4302(1)	-794(1)	8285(1)	36(1)
C(38)	3667(1)	3395(1)	10188(1)	14(1)
C(39)	4197(1)	3696(1)	10815(1)	18(1)
C(40)	3975(1)	3004(1)	11346(1)	25(1)
C(41)	5312(1)	3695(1)	10719(1)	29(1)
C(42)	3866(1)	4743(1)	10972(1)	25(1)

Table 3. Bond lengths [Å] and angles [°] for 1.45.

Ru(1)-O(1)	2.3263(6)
Ru(1)-O(2)	2.1091(6)
Ru(1)-O(3)	2.3680(6)
Ru(1)-O(4)	2.0318(6)
Ru(1)-C(1)	1.9661(7)
Ru(1)-C(23)	1.8397(8)
O(1)-C(29)	1.3791(10)
O(1)-C(30)	1.4722(10)
O(2)-C(33)	1.2810(9)
O(3)-C(33)	1.2526(10)
O(4)-C(38)	1.2975(10)
O(5)-C(38)	1.2275(10)
N(1)-C(1)	1.3746(10)
N(1)-C(2)	1.4675(10)
N(1)-C(4)	1.4578(10)
N(2)-C(1)	1.3602(10)
N(2)-C(3)	1.4721(10)
N(2)-C(11)	1.4350(10)
C(2)-H(2A)	0.962(14)
C(2)-H(2B)	0.984(12)
C(2)-C(3)	1.5096(12)
C(3)-H(3A)	0.969(12)
C(3)-H(3B)	0.922(12)
C(4)-H(4A)	0.958(11)
C(4)-H(4B)	0.953(13)
C(4)-C(5)	1.5100(11)
C(5)-C(6)	1.3912(12)
C(5)-C(10)	1.3963(11)
C(6)-H(6)	0.952(14)
C(6)-C(7)	1.3918(13)
C(7)-H(7)	0.953(14)
C(7)-C(8)	1.3879(14)
C(8)-H(8)	0.967(13)
C(8)-C(9)	1.3845(15)
C(9)-H(9)	0.936(15)
C(9)-C(10)	1.3923(13)
C(10)-H(10)	0.931(12)
C(11)-C(12)	1.4104(12)
C(11)-C(16)	1.4056(12)
C(12)-C(13)	1.3965(12)

C(12)-C(17)	1.5138(13)
C(13)-H(13)	0.964(13)
C(13)-C(14)	1.3843(15)
C(14)-H(14)	0.964(14)
C(14)-C(15)	1.3847(16)
C(15)-H(15)	0.970(15)
C(15)-C(16)	1.3981(12)
C(16)-C(20)	1.5146(13)
C(17)-H(17)	0.962(12)
C(17)-C(18)	1.5367(15)
C(17)-C(19)	1.5296(13)
C(18)-H(18A)	0.962(14)
C(18)-H(18B)	0.969(15)
C(18)-H(18C)	1.016(14)
C(19)-H(19A)	0.928(17)
C(19)-H(19B)	0.966(16)
C(19)-H(19C)	0.897(17)
C(20)-H(20)	0.965(13)
C(20)-C(21)	1.5352(13)
C(20)-C(22)	1.5327(15)
C(21)-H(21A)	0.914(15)
C(21)-H(21B)	0.983(14)
C(21)-H(21C)	0.937(14)
C(22)-H(22A)	0.886(15)
C(22)-H(22B)	0.944(15)
C(22)-H(22C)	1.086(15)
C(23)-C(24)	1.4519(11)
C(23)-H(23)	0.933(15)
C(24)-C(25)	1.4029(11)
C(24)-C(29)	1.4038(11)
C(25)-H(25)	0.970(12)
C(25)-C(26)	1.3849(12)
C(26)-H(26)	0.903(14)
C(26)-C(27)	1.3933(13)
C(27)-H(27)	0.980(14)
C(27)-C(28)	1.3937(13)
C(28)-H(28)	0.976(13)
C(28)-C(29)	1.3904(11)
C(30)-H(30)	0.960(12)
C(30)-C(31)	1.5156(15)
C(30)-C(32)	1.5003(15)
C(31)-H(31A)	0.880(16)
C(31)-H(31B)	0.976(15)
C(31)-H(31C)	1.003(17)
C(32)-H(32A)	0.923(11)
C(32)-H(32B)	0.960(18)
C(32)-H(32C)	0.971(17)
C(33)-C(34)	1.5248(11)
C(34)-C(35)	1.5324(15)
C(34)-C(36)	1.5199(14)
C(34)-C(37)	1.5239(14)

C(35)-H(35A)	0.990(18)
C(35)-H(35B)	1.034(15)
C(35)-H(35C)	0.961(18)
C(36)-H(36A)	0.999(17)
C(36)-H(36B)	0.947(16)
C(36)-H(36C)	0.98(2)
C(37)-H(37A)	1.037(18)
C(37)-H(37B)	0.970(17)
C(37)-H(37C)	1.103(18)
C(38)-C(39)	1.5402(12)
C(39)-C(40)	1.5221(13)
C(39)-C(41)	1.5383(14)
C(39)-C(42)	1.5365(13)
C(40)-H(40A)	1.003(14)
C(40)-H(40B)	1.018(16)
C(40)-H(40C)	0.941(15)
C(41)-H(41A)	0.991(13)
C(41)-H(41B)	1.076(17)
C(41)-H(41C)	1.029(16)
C(42)-H(42A)	1.017(15)
C(42)-H(42B)	1.034(14)
C(42)-H(42C)	1.080(17)

O(1)-Ru(1)-O(3)	95.20(2)
O(2)-Ru(1)-O(1)	87.31(2)
O(2)-Ru(1)-O(3)	58.18(2)
O(4)-Ru(1)-O(1)	84.72(2)
O(4)-Ru(1)-O(2)	158.41(2)
O(4)-Ru(1)-O(3)	102.60(2)
C(1)-Ru(1)-O(1)	175.56(2)
C(1)-Ru(1)-O(2)	92.34(3)
C(1)-Ru(1)-O(3)	88.36(3)
C(1)-Ru(1)-O(4)	97.10(3)
C(23)-Ru(1)-O(1)	78.79(3)
C(23)-Ru(1)-O(2)	99.49(3)
C(23)-Ru(1)-O(3)	157.36(3)
C(23)-Ru(1)-O(4)	98.59(3)
C(23)-Ru(1)-C(1)	96.91(3)
C(29)-O(1)-Ru(1)	108.71(4)
C(29)-O(1)-C(30)	117.29(6)
C(30)-O(1)-Ru(1)	131.95(5)
C(33)-O(2)-Ru(1)	96.72(5)
C(33)-O(3)-Ru(1)	85.60(5)
C(38)-O(4)-Ru(1)	125.85(5)
C(1)-N(1)-C(2)	110.94(6)
C(1)-N(1)-C(4)	123.39(7)
C(4)-N(1)-C(2)	115.19(6)
C(1)-N(2)-C(3)	112.30(6)
C(1)-N(2)-C(11)	131.17(6)
C(11)-N(2)-C(3)	116.51(6)
N(1)-C(1)-Ru(1)	121.88(5)

N(2)-C(1)-Ru(1)	131.70(5)
N(2)-C(1)-N(1)	106.12(6)
N(1)-C(2)-H(2A)	109.8(8)
N(1)-C(2)-H(2B)	107.8(7)
N(1)-C(2)-C(3)	101.35(6)
H(2A)-C(2)-H(2B)	110.2(11)
C(3)-C(2)-H(2A)	116.1(8)
C(3)-C(2)-H(2B)	111.0(7)
N(2)-C(3)-C(2)	101.18(7)
N(2)-C(3)-H(3A)	110.7(7)
N(2)-C(3)-H(3B)	111.7(8)
C(2)-C(3)-H(3A)	115.7(7)
C(2)-C(3)-H(3B)	111.4(8)
H(3A)-C(3)-H(3B)	106.1(10)
N(1)-C(4)-H(4A)	112.1(7)
N(1)-C(4)-H(4B)	108.3(8)
N(1)-C(4)-C(5)	112.83(7)
H(4A)-C(4)-H(4B)	106.7(10)
C(5)-C(4)-H(4A)	108.3(7)
C(5)-C(4)-H(4B)	108.3(8)
C(6)-C(5)-C(4)	122.11(7)
C(6)-C(5)-C(10)	118.82(8)
C(10)-C(5)-C(4)	119.04(8)
C(5)-C(6)-H(6)	121.0(8)
C(5)-C(6)-C(7)	120.51(8)
C(7)-C(6)-H(6)	118.5(8)
C(6)-C(7)-H(7)	119.9(9)
C(8)-C(7)-C(6)	120.23(9)
C(8)-C(7)-H(7)	119.9(9)
C(7)-C(8)-H(8)	119.5(8)
C(9)-C(8)-C(7)	119.76(9)
C(9)-C(8)-H(8)	120.8(8)
C(8)-C(9)-H(9)	120.5(9)
C(8)-C(9)-C(10)	120.07(8)
C(10)-C(9)-H(9)	119.4(9)
C(5)-C(10)-H(10)	120.0(8)
C(9)-C(10)-C(5)	120.61(9)
C(9)-C(10)-H(10)	119.4(8)
C(12)-C(11)-N(2)	117.87(7)
C(16)-C(11)-N(2)	119.95(7)
C(16)-C(11)-C(12)	122.03(7)
C(11)-C(12)-C(17)	122.96(7)
C(13)-C(12)-C(11)	117.73(8)
C(13)-C(12)-C(17)	119.30(8)
C(12)-C(13)-H(13)	118.6(8)
C(14)-C(13)-C(12)	121.19(9)
C(14)-C(13)-H(13)	120.2(8)
C(13)-C(14)-H(14)	120.8(8)
C(13)-C(14)-C(15)	120.02(8)
C(15)-C(14)-H(14)	119.1(8)
C(14)-C(15)-H(15)	118.4(9)

C(14)-C(15)-C(16)	121.43(9)
C(16)-C(15)-H(15)	120.1(9)
C(11)-C(16)-C(20)	122.60(7)
C(15)-C(16)-C(11)	117.53(8)
C(15)-C(16)-C(20)	119.87(8)
C(12)-C(17)-H(17)	109.6(7)
C(12)-C(17)-C(18)	111.44(8)
C(12)-C(17)-C(19)	111.28(8)
C(18)-C(17)-H(17)	106.0(7)
C(19)-C(17)-H(17)	108.2(7)
C(19)-C(17)-C(18)	110.11(9)
C(17)-C(18)-H(18A)	115.4(9)
C(17)-C(18)-H(18B)	110.7(9)
C(17)-C(18)-H(18C)	112.5(8)
H(18A)-C(18)-H(18B)	103.4(12)
H(18A)-C(18)-H(18C)	106.1(11)
H(18B)-C(18)-H(18C)	108.0(12)
C(17)-C(19)-H(19A)	112.8(9)
C(17)-C(19)-H(19B)	109.2(9)
C(17)-C(19)-H(19C)	113.5(11)
H(19A)-C(19)-H(19B)	110.2(13)
H(19A)-C(19)-H(19C)	104.1(14)
H(19B)-C(19)-H(19C)	106.8(13)
C(16)-C(20)-H(20)	109.9(7)
C(16)-C(20)-C(21)	111.21(8)
C(16)-C(20)-C(22)	111.13(9)
C(21)-C(20)-H(20)	104.8(7)
C(22)-C(20)-H(20)	109.2(8)
C(22)-C(20)-C(21)	110.44(8)
C(20)-C(21)-H(21A)	109.6(9)
C(20)-C(21)-H(21B)	111.9(8)
C(20)-C(21)-H(21C)	112.9(8)
H(21A)-C(21)-H(21B)	107.4(12)
H(21A)-C(21)-H(21C)	108.5(12)
H(21B)-C(21)-H(21C)	106.2(12)
C(20)-C(22)-H(22A)	112.3(10)
C(20)-C(22)-H(22B)	110.9(9)
C(20)-C(22)-H(22C)	113.7(8)
H(22A)-C(22)-H(22B)	104.9(14)
H(22A)-C(22)-H(22C)	108.2(12)
H(22B)-C(22)-H(22C)	106.4(12)
Ru(1)-C(23)-H(23)	127.4(9)
C(24)-C(23)-Ru(1)	119.19(5)
C(24)-C(23)-H(23)	113.3(9)
C(25)-C(24)-C(23)	122.12(7)
C(25)-C(24)-C(29)	118.62(7)
C(29)-C(24)-C(23)	119.24(7)
C(24)-C(25)-H(25)	116.0(7)
C(26)-C(25)-C(24)	120.90(8)
C(26)-C(25)-H(25)	123.1(7)
C(25)-C(26)-H(26)	121.2(8)

C(25)-C(26)-C(27)	119.42(8)
C(27)-C(26)-H(26)	119.3(8)
C(26)-C(27)-H(27)	121.5(8)
C(26)-C(27)-C(28)	121.03(8)
C(28)-C(27)-H(27)	117.4(8)
C(27)-C(28)-H(28)	118.8(8)
C(29)-C(28)-C(27)	119.04(8)
C(29)-C(28)-H(28)	122.1(8)
O(1)-C(29)-C(24)	113.83(6)
O(1)-C(29)-C(28)	125.16(7)
C(28)-C(29)-C(24)	120.98(7)
O(1)-C(30)-H(30)	103.8(7)
O(1)-C(30)-C(31)	109.78(8)
O(1)-C(30)-C(32)	107.15(7)
C(31)-C(30)-H(30)	112.9(7)
C(32)-C(30)-H(30)	110.9(7)
C(32)-C(30)-C(31)	111.86(10)
C(30)-C(31)-H(31A)	108.2(11)
C(30)-C(31)-H(31B)	106.3(8)
C(30)-C(31)-H(31C)	110.3(10)
H(31A)-C(31)-H(31B)	107.1(13)
H(31A)-C(31)-H(31C)	114.7(14)
H(31B)-C(31)-H(31C)	109.9(13)
C(30)-C(32)-H(32A)	106.2(7)
C(30)-C(32)-H(32B)	107.6(11)
C(30)-C(32)-H(32C)	114.8(10)
H(32A)-C(32)-H(32B)	109.3(13)
H(32A)-C(32)-H(32C)	107.1(12)
H(32B)-C(32)-H(32C)	111.6(14)
O(2)-C(33)-C(34)	118.71(7)
O(3)-C(33)-O(2)	119.48(7)
O(3)-C(33)-C(34)	121.80(7)
C(33)-C(34)-C(35)	107.73(8)
C(36)-C(34)-C(33)	109.82(7)
C(36)-C(34)-C(35)	109.15(10)
C(36)-C(34)-C(37)	110.99(10)
C(37)-C(34)-C(33)	109.98(8)
C(37)-C(34)-C(35)	109.11(9)
C(34)-C(35)-H(35A)	113.0(10)
C(34)-C(35)-H(35B)	109.8(8)
C(34)-C(35)-H(35C)	112.9(11)
H(35A)-C(35)-H(35B)	108.3(13)
H(35A)-C(35)-H(35C)	106.1(14)
H(35B)-C(35)-H(35C)	106.5(13)
C(34)-C(36)-H(36A)	107.2(10)
C(34)-C(36)-H(36B)	109.9(10)
C(34)-C(36)-H(36C)	111.8(11)
H(36A)-C(36)-H(36B)	112.5(13)
H(36A)-C(36)-H(36C)	108.3(14)
H(36B)-C(36)-H(36C)	107.2(15)
C(34)-C(37)-H(37A)	109.3(10)

C(34)-C(37)-H(37B)	107.7(10)
C(34)-C(37)-H(37C)	110.3(9)
H(37A)-C(37)-H(37B)	112.7(14)
H(37A)-C(37)-H(37C)	106.8(14)
H(37B)-C(37)-H(37C)	110.0(13)
O(4)-C(38)-C(39)	115.34(7)
O(5)-C(38)-O(4)	125.81(8)
O(5)-C(38)-C(39)	118.80(7)
C(40)-C(39)-C(38)	112.72(7)
C(40)-C(39)-C(41)	110.09(9)
C(40)-C(39)-C(42)	109.54(8)
C(41)-C(39)-C(38)	106.81(7)
C(42)-C(39)-C(38)	108.13(8)
C(42)-C(39)-C(41)	109.47(8)
C(39)-C(40)-H(40A)	107.9(7)
C(39)-C(40)-H(40B)	106.8(8)
C(39)-C(40)-H(40C)	110.1(10)
H(40A)-C(40)-H(40B)	113.6(12)
H(40A)-C(40)-H(40C)	110.4(12)
H(40B)-C(40)-H(40C)	107.9(12)
C(39)-C(41)-H(41A)	106.7(8)
C(39)-C(41)-H(41B)	109.0(9)
C(39)-C(41)-H(41C)	112.6(9)
H(41A)-C(41)-H(41B)	105.3(12)
H(41A)-C(41)-H(41C)	114.4(12)
H(41B)-C(41)-H(41C)	108.5(12)
C(39)-C(42)-H(42A)	112.7(8)
C(39)-C(42)-H(42B)	110.0(8)
C(39)-C(42)-H(42C)	111.1(9)
H(42A)-C(42)-H(42B)	104.4(11)
H(42A)-C(42)-H(42C)	109.2(12)
H(42B)-C(42)-H(42C)	109.2(11)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for 1.45. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	88(1)	93(1)	90(1)	10(1)	13(1)	-4(1)
O(1)	122(2)	144(2)	141(2)	50(2)	27(2)	21(2)
O(2)	113(2)	127(2)	136(2)	-9(2)	12(2)	-5(2)
O(3)	121(2)	151(2)	176(3)	-12(2)	8(2)	-1(2)
O(4)	164(2)	146(2)	121(2)	6(2)	-8(2)	-24(2)
O(5)	263(3)	141(2)	169(3)	7(2)	-15(2)	-5(2)
N(1)	92(2)	140(2)	132(3)	37(2)	21(2)	-11(2)
N(2)	96(2)	132(2)	130(3)	43(2)	15(2)	-1(2)

C(1)	97(3)	103(3)	107(3)	-2(2)	9(2)	-4(2)
C(2)	129(3)	183(3)	208(4)	82(3)	35(3)	-18(3)
C(3)	148(3)	205(3)	169(4)	91(3)	26(3)	-6(3)
C(4)	100(3)	166(3)	134(3)	3(2)	7(2)	-12(2)
C(5)	99(3)	144(3)	156(3)	33(2)	21(2)	-6(2)
C(6)	133(3)	209(4)	157(3)	10(3)	19(3)	7(3)
C(7)	198(4)	262(4)	188(4)	11(3)	56(3)	44(3)
C(8)	156(3)	268(4)	265(5)	76(3)	88(3)	48(3)
C(9)	102(3)	255(4)	296(5)	67(4)	28(3)	3(3)
C(10)	110(3)	208(4)	214(4)	24(3)	1(3)	-22(3)
C(11)	101(3)	148(3)	155(3)	62(2)	4(2)	6(2)
C(12)	142(3)	147(3)	188(4)	66(3)	27(3)	28(2)
C(13)	161(3)	192(4)	314(5)	71(3)	44(3)	61(3)
C(14)	124(3)	254(4)	397(6)	114(4)	10(3)	41(3)
C(15)	120(3)	249(4)	313(5)	86(4)	-38(3)	-12(3)
C(16)	126(3)	182(3)	186(4)	67(3)	-21(3)	-14(2)
C(17)	185(4)	151(3)	233(4)	12(3)	21(3)	33(3)
C(18)	332(5)	289(5)	251(5)	-48(4)	42(4)	54(4)
C(19)	294(5)	162(4)	397(6)	39(4)	15(4)	-2(3)
C(20)	160(3)	220(4)	199(4)	8(3)	-25(3)	-39(3)
C(21)	200(4)	211(4)	344(6)	27(4)	-25(4)	-48(3)
C(22)	389(6)	388(6)	203(5)	1(4)	-29(4)	-108(5)
C(23)	128(3)	116(3)	131(3)	23(2)	30(2)	11(2)
C(24)	129(3)	114(3)	130(3)	7(2)	43(2)	-2(2)
C(25)	143(3)	151(3)	204(4)	12(3)	69(3)	18(2)
C(26)	156(3)	201(4)	249(4)	-1(3)	105(3)	-1(3)
C(27)	208(4)	189(3)	205(4)	13(3)	108(3)	-38(3)
C(28)	194(3)	148(3)	163(3)	28(3)	64(3)	-19(3)
C(29)	137(3)	121(3)	120(3)	9(2)	34(2)	-8(2)
C(30)	179(3)	187(3)	207(4)	106(3)	11(3)	31(3)
C(31)	363(6)	282(5)	239(5)	87(4)	-111(4)	-74(4)
C(32)	261(5)	441(7)	425(7)	275(6)	128(5)	183(5)
C(33)	135(3)	123(3)	122(3)	10(2)	34(2)	-3(2)
C(34)	170(3)	161(3)	180(4)	-42(3)	65(3)	-11(3)
C(35)	461(7)	359(6)	175(5)	-63(4)	29(4)	-5(5)
C(36)	535(8)	220(4)	573(9)	-194(5)	404(7)	-171(5)
C(37)	285(5)	401(6)	402(7)	-181(5)	13(5)	152(5)
C(38)	141(3)	157(3)	131(3)	-11(2)	15(2)	-2(2)
C(39)	207(4)	192(3)	137(3)	-21(3)	-3(3)	-35(3)
C(40)	360(5)	229(4)	146(4)	3(3)	-17(4)	-39(4)
C(41)	190(4)	421(6)	261(5)	-49(4)	-17(4)	-41(4)
C(42)	343(5)	187(4)	208(4)	-52(3)	18(4)	-46(3)

Table 5. Hydrogen coordinates (x 10^3) and isotropic displacement parameters ($Å^2$x 10^3) for 1.45.

	x	y	z	U_{iso}
H(2A)	446(1)	373(1)	790(1)	26(3)
H(2B)	414(1)	438(1)	847(1)	17(3)
H(3A)	268(1)	458(1)	785(1)	19(3)
H(3B)	282(1)	360(1)	754(1)	16(3)
H(4A)	467(1)	222(1)	928(1)	9(2)
H(4B)	498(1)	329(1)	921(1)	23(3)
H(6)	485(1)	179(1)	786(1)	23(3)
H(7)	619(1)	126(1)	733(1)	31(4)
H(8)	781(1)	154(1)	774(1)	24(3)
H(9)	805(1)	237(1)	870(1)	37(4)
H(10)	671(1)	288(1)	923(1)	16(3)
H(13)	-18(1)	528(1)	893(1)	27(3)
H(14)	-135(1)	427(1)	838(1)	32(4)
H(15)	-84(1)	295(1)	780(1)	33(4)
H(17)	242(1)	486(1)	910(1)	13(3)
H(18A)	88(1)	550(1)	985(1)	31(4)
H(18B)	198(1)	564(1)	1002(1)	35(4)
H(18C)	153(1)	455(1)	1000(1)	28(3)
H(19A)	195(1)	616(1)	839(1)	42(4)
H(19B)	228(1)	656(1)	905(1)	35(4)
H(19C)	122(1)	649(1)	881(1)	45(4)
H(20)	162(1)	198(1)	782(1)	16(3)
H(21A)	34(1)	117(1)	826(1)	30(4)
H(21B)	57(1)	66(1)	765(1)	33(4)
H(21C)	-34(1)	132(1)	769(1)	30(4)
H(22A)	28(1)	249(1)	684(1)	36(4)
H(22B)	108(1)	181(1)	676(1)	36(4)
H(22C)	136(1)	297(1)	685(1)	32(4)
H(25)	-43(1)	260(1)	982(1)	20(3)
H(26)	-139(1)	165(1)	1048(1)	23(3)
H(27)	-73(1)	27(1)	1102(1)	31(4)
H(28)	89(1)	-19(1)	1089(1)	22(3)
H(30)	230(1)	-53(1)	1056(1)	16(3)
H(31A)	322(1)	106(1)	1116(1)	44(4)
H(31B)	332(1)	6(1)	1144(1)	33(4)
H(31C)	225(1)	60(1)	1140(1)	51(5)
H(32A)	349(1)	-52(1)	991(1)	7(2)
H(32B)	405(1)	-60(1)	1055(1)	59(5)
H(32C)	403(1)	40(1)	1015(1)	48(5)
H(35A)	237(1)	26(1)	747(1)	50(5)
H(35B)	314(1)	-56(1)	722(1)	40(4)
H(35C)	349(1)	52(1)	745(1)	56(5)
H(36A)	265(1)	-146(1)	876(1)	41(4)
H(36B)	256(1)	-172(1)	802(1)	42(4)

H(36C)	183(2)	-98(1)	828(1)	66(6)
H(37A)	479(1)	-22(1)	821(1)	61(5)
H(37B)	436(1)	-133(1)	799(1)	48(4)
H(37C)	447(1)	-105(1)	877(1)	56(5)
H(40A)	324(1)	300(1)	1139(1)	22(3)
H(40B)	437(1)	325(1)	1174(1)	37(4)
H(40C)	420(1)	237(1)	1126(1)	39(4)
H(41A)	549(1)	301(1)	1061(1)	24(3)
H(41B)	571(1)	385(1)	1116(1)	46(4)
H(41C)	550(1)	421(1)	1040(1)	43(4)
H(42A)	403(1)	524(1)	1064(1)	34(4)
H(42B)	425(1)	499(1)	1138(1)	32(4)
H(42C)	308(1)	477(1)	1104(1)	50(5)
H(23)	109(1)	286(1)	937(1)	32(4)

Table 6. Hydrogen bonds for 1.45 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(4)-H(4A)...O(3)	0.958(11)	2.313(11)	2.9217(10)	120.8(8)
C(4)-H(4A)...O(4)	0.958(11)	2.610(11)	3.2182(10)	121.7(8)
C(4)-H(4B)...O(5)	0.953(13)	2.562(13)	3.0446(11)	111.6(10)
C(32)-H(32C)...O(3)	0.971(17)	2.555(17)	3.0726(14)	113.4(12)

Symmetry transformations used to generate equivalent atoms:

Appendix B

THE CARTESIAN COORDINATES (Å), SCF ENERGIES, ENTHALPIES AT 298K, AND GIBBS FREE ENERGIES AT 298K FOR OPTIMIZED STRUCTURES (CHAPTER 1)

B3LYP absolute calculation energies, M06 single point energies, correction of enthalpies, and correction of free energies (in a.u.).

Geometry	$E_{(B3LYP)}$	$E_{(M06)}$	$H_{(correction)}$	$G_{(correction)}$	IF*
1.5	-1869.154870	-1869.355471	0.851468	0.732251	-
1.18	-3807.213242	-3807.642829	1.581637	1.379476	-
1.25-ts	-1869.109930	-1869.308906	0.850440	0.733084	-406.6
1.26	-1869.157877	-1869.360963	0.851478	0.733117	-
1.27-ts	-1869.154881	-1869.362400	0.848143	0.732290	-661.2
1.28	-1869.170526	-1869.379691	0.850013	0.733130	-
1.31-ts	-1869.137940	-1869.340957	0.846074	0.727457	-894.9
1.32	-1869.139490	-1869.345785	0.850344	0.730582	-
1.33	-2250.633517	-2250.733011	0.946725	0.815367	-
1.34	-1903.590978	-1903.790084	0.789309	0.673263	-
1.29-ts	-1869.103133	-1869.304905	0.847336	0.728820	-1017.3
1.30	-1869.129801	-1869.325086	0.849969	0.730747	-
1.35	-1522.085093	-1522.391995	0.692955	0.593140	-
Piv-OH	-347.017538	-346.906507	0.156655	0.115014	-
Benzoquinone	-381.444419	-381.307355	0.092618	0.054941	-

* IF: The imaginary frequencies for the transition states.

B3LYP geometries for optimized compounds and transition states.

1.5

Ru	-0.36138100	0.19922600	-0.08343200
O	-1.45322500	2.42938300	-0.13980700
O	0.94525000	0.37233600	-2.15367700
O	1.61592600	1.28490200	-0.25998100
N	-0.68223600	-2.64370400	0.12967400
N	1.31696800	-2.19228200	0.91703800
C	0.21067400	-1.64693000	0.33852400
C	-0.24462200	-3.95267000	0.61528500
H	-0.19643900	-4.68095900	-0.20311200
H	-0.93412600	-4.34415400	1.37219000
C	1.14410400	-3.63280100	1.20731100
H	1.19036000	-3.80391600	2.28961200
H	1.94227300	-4.22068800	0.74500800
C	-2.02900700	-2.31210300	-0.33747500
C	-3.02438900	-2.30470800	0.85088100
H	-2.64854700	-1.64076300	1.63484800
H	-3.09532300	-3.31504600	1.28034500
C	-4.41156800	-1.83341000	0.37875600
H	-5.10367600	-1.82959500	1.23168900
C	-4.93150500	-2.79450100	-0.70852700
H	-5.04647300	-3.80689400	-0.29504900
H	-5.92452900	-2.47578000	-1.05400800
C	-3.94243200	-2.80857200	-1.89230100

H	-4.30759400	-3.49275200	-2.66992300
C	-2.55766100	-3.30156500	-1.40348600
H	-1.84947300	-3.35207600	-2.24100700
H	-2.65476300	-4.31813900	-0.99251000
C	-3.83657400	-1.37844800	-2.46761500
H	-3.17213000	-1.36713800	-3.34196200
H	-4.82764800	-1.04967100	-2.81328000
C	-3.29409100	-0.41278400	-1.37964500
H	-3.22337000	0.59746400	-1.79818100
C	-1.89293800	-0.91431200	-0.98306800
H	-1.32610700	-1.05628400	-1.92178100
C	-4.27508700	-0.40665100	-0.19057600
H	-3.91918500	0.27443900	0.59089600
H	-5.25795000	-0.03962000	-0.51938600
C	2.62852700	-1.62149200	1.04480900
C	2.99558400	-0.94374200	2.21820800
C	4.31687400	-0.49867400	2.34370700
H	4.60614100	0.02842900	3.25058500
C	5.27045800	-0.71665800	1.34721300
C	4.87384000	-1.40253800	0.19337800
H	5.60338100	-1.58913200	-0.59234900
C	3.56381400	-1.85635500	0.01712400
C	2.00205200	-0.67255000	3.32031800
H	2.51431400	-0.37841100	4.24178800
H	1.38022700	-1.54778500	3.53919800
H	1.32466300	0.13947800	3.03322400

C	6.68553900	-0.20727900	1.49646300
H	6.81340600	0.75757600	0.98791500
H	7.41130200	-0.90187100	1.05874000
H	6.94938500	-0.05874300	2.54880600
C	3.16707600	-2.56086800	-1.26076900
H	2.82036000	-3.58646200	-1.08359600
H	4.01735000	-2.62083000	-1.94636100
H	2.35844600	-2.02525800	-1.77018500
C	-1.05689500	0.41292300	1.62902800
H	-0.95871600	-0.31376100	2.44623200
C	-1.74062500	1.62865300	2.04779500
C	-2.22857100	1.79880100	3.35771900
H	-2.08890700	0.98606000	4.06686800
C	-2.86848700	2.97035800	3.75267300
H	-3.23473200	3.08105100	4.76918000
C	-3.02505200	4.00414700	2.82865200
H	-3.51500600	4.92916100	3.12038500
C	-2.55405100	3.87237800	1.51803600
H	-2.68574100	4.69753400	0.82931700
C	-1.92465600	2.68915600	1.12575700
C	-1.37023500	3.51879500	-1.10898400
H	-2.29415200	4.10071100	-1.02209000
C	-1.33912200	2.89764500	-2.49862500
H	-0.50305300	2.20497800	-2.62092000
H	-1.24767800	3.69549400	-3.24438500
H	-2.26736700	2.35341400	-2.69656600

C	-0.15952000	4.38987800	-0.78326800
H	-0.26410000	4.86544500	0.19698700
H	-0.04697300	5.17893300	-1.53536500
H	0.74452100	3.77576500	-0.76479000
C	1.78068400	1.07076700	-1.50652700
C	2.98506500	1.70019800	-2.24524000
C	3.74900600	0.59116800	-2.99678400
H	3.07603500	0.03628400	-3.65662000
H	4.20838100	-0.11321700	-2.29679600
H	4.54991600	1.03208000	-3.60360400
C	2.44547500	2.70613900	-3.28656600
H	1.76813300	2.21183100	-3.98974300
H	3.27876300	3.13822600	-3.85445100
H	1.90520400	3.53179700	-2.81057900
C	3.92588600	2.41470100	-1.26195100
H	4.77953700	2.84193900	-1.80386900
H	4.30633800	1.72128800	-0.50583900
H	3.41391700	3.22598800	-0.73515500

1.18

C	-3.87618100	1.24198900	0.28221400
C	-6.18053600	1.76130300	0.22296800
C	-5.38875100	2.93669500	-0.35869500
C	-5.38273800	-0.56133700	0.99304400
C	-7.17131700	-2.48840700	2.37380900
C	-6.77045000	-2.66763800	0.89580100

C	-6.55068800	-1.27831200	0.26199000
C	-5.47150800	-3.49359300	0.80453600
C	-4.32201300	-2.75923700	1.55562000
C	-4.11315500	-1.41959200	0.81937600
C	-3.46678500	-1.41453300	-0.46728900
C	-2.86036600	-2.58526600	-1.15924100
C	-1.97053900	-3.50227600	-0.57870100
C	-1.46481800	-4.60168800	-1.27572900
C	-1.82443600	-4.79846700	-2.60544400
C	-2.68919600	-3.89822000	-3.23005000
C	-3.20968000	-2.80854500	-2.52275700
C	-4.45066800	-1.96578300	-4.45895300
C	-5.74928100	-1.17442200	-4.58144000
C	-3.33120200	-1.38931900	-5.32751100
C	3.87373900	1.24471100	-0.28472600
C	6.17761100	1.76707800	-0.22784400
C	5.38431900	2.94397900	0.34910600
C	5.38206600	-0.55753600	-0.99456900
C	5.74925900	-0.40620200	-2.49438100
C	6.02721500	-1.78212400	-3.12655100
C	7.17224900	-2.48464400	-2.37326900
C	6.77231700	-2.66201200	-0.89478600
C	6.55121500	-1.27196200	-0.26297200
C	5.47440100	-3.48936600	-0.80170000
C	4.32365600	-2.75754400	-1.55334500
C	4.11349500	-1.41696100	-0.81902000

C	4.74144200	-2.61981000	-3.03059800
C	2.99609700	3.41335000	0.71821300
C	2.54812500	4.51176100	-0.03223200
C	2.95171300	4.69499900	-1.47693500
C	3.46767800	-1.41129300	0.46802000
C	2.08576900	-0.31103300	-3.41671200
C	1.99135400	1.02058100	-2.82806200
C	0.92970900	1.36722000	-1.96248500
C	-0.07269900	0.39116100	-1.55775300
C	0.36460200	-0.98628700	-1.69538000
C	1.44059100	-1.30617200	-2.52995200
H	-6.96469800	1.40586900	-0.45105900
H	-6.64548000	2.01158400	1.18497700
H	-5.57479000	3.07483400	-1.43031500
H	-7.47659300	-0.69132000	0.34716400
H	-6.30800500	-1.36872800	-0.80390500
H	-5.62660200	-4.48116000	1.26094100
H	-5.19738800	-3.66040100	-0.24309800
H	-3.42257200	-3.37233100	1.49475500
H	-3.91539800	-0.75169000	-1.19830500
H	-1.64250900	-3.33563800	0.44068600
H	-0.78983300	-5.29353400	-0.78141800
H	-1.43375700	-5.64269100	-3.16703900
H	-2.95407700	-4.05920900	-4.26809600
H	-4.64966500	-3.00866800	-4.74031700
H	-5.59201500	-0.13423200	-4.27502000

H	-6.10308700	-1.17999400	-5.61813000
H	-6.52666800	-1.60886900	-3.94499400
H	-2.39067300	-1.92892700	-5.18585200
H	-3.60295100	-1.44748400	-6.38781000
H	-3.16071600	-0.33812600	-5.07070900
H	6.64411900	2.01463900	-1.18974000
H	5.59050700	3.89109400	-0.15811200
H	6.63962100	0.23199700	-2.58544100
H	4.92633600	0.08584200	-3.02291700
H	6.30040700	-1.64245900	-4.18019400
H	8.09975800	-1.89775000	-2.44566600
H	7.37710500	-3.46333700	-2.82814700
H	7.57626700	-3.17564300	-0.35052700
H	7.47637500	-0.68398600	-0.34949000
H	5.63048600	-4.47741900	-1.25673000
H	5.20098100	-3.65498200	0.24630300
H	3.42494100	-3.37159000	-1.49097700
H	4.91996600	-3.62569600	-3.43796600
H	3.95813400	-2.15732600	-3.63407400
H	4.01618000	4.94813300	-1.57288200
H	2.78898200	3.78629800	-2.06301200
H	2.38255300	5.50754700	-1.93768500
H	2.63928700	1.79184400	-3.23560300
H	0.76287500	2.39614000	-1.66332400
H	-0.22389200	-1.76317400	-1.22449700
H	1.68942000	-2.34947000	-2.70073600

N	-5.13039000	0.75368300	0.40306100
N	-3.97990600	2.53314800	-0.14136500
N	5.12843100	0.75819400	-0.40665000
N	3.97580400	2.53672700	0.13653500
O	-4.10002700	-1.91643100	-3.06596000
O	1.14796800	0.75359700	0.99238100
O	2.73640000	-0.59095800	-4.43269900
O	-1.14939800	0.75264800	-0.99403200
Ru	-2.33624200	-0.01630300	0.79036400
Ru	2.33511300	-0.01591200	-0.79083000
C	1.74713100	5.47052000	0.60063600
H	1.40468900	6.32756000	0.02576500
C	2.66906500	3.27995900	2.08315100
C	1.40185000	5.36855800	1.94928800
C	1.86470300	4.26043700	2.66815400
H	1.60984200	4.16541200	3.72186700
C	3.18863700	2.13286100	2.91547600
H	2.82233300	1.17819600	2.53004800
H	4.28544900	2.09190700	2.92232000
H	2.85800300	2.23528900	3.95397100
C	0.58636400	6.44049700	2.63539200
H	1.18548700	6.97804000	3.38188400
H	0.21217300	7.18068800	1.92068600
H	-0.27440200	6.01514900	3.16505800
H	5.57196900	3.08839200	1.41960200
H	6.96083500	1.41401600	0.44856400

H	3.91586000	-0.74716300	1.19813500
C	2.86294700	-2.58216500	1.16123200
C	3.21395500	-2.80480300	2.52440400
C	1.97296500	-3.49984900	0.58199400
C	2.69473100	-3.89440700	3.23270400
C	1.46860000	-4.59928000	1.27999000
H	1.64387900	-3.33373500	-0.43716200
C	1.82974300	-4.79531300	2.60938200
H	2.96077400	-4.05487800	4.27051700
H	0.79345200	-5.29166600	0.78666600
H	1.44007900	-5.63948200	3.17174300
O	4.10448700	-1.91197200	3.06615700
C	4.45931300	-1.96238500	4.45796000
H	4.65829300	-3.00560300	4.73810300
C	5.75891300	-1.17207900	4.57699200
H	5.60166900	-0.13194200	4.27037200
H	6.11516600	-1.17734500	5.61283500
H	6.53447900	-1.60740900	3.93892800
C	3.34298600	-1.38548300	5.33031300
H	3.61787600	-1.44465000	6.38974000
H	3.17269900	-0.33395100	5.07476300
H	2.40152000	-1.92407400	5.19108600
C	-3.00049600	3.41211600	-0.72001200
C	-2.66966300	3.28074300	-2.08405400
C	-2.55605700	4.51040500	0.03296300
C	-1.86478200	4.26300500	-2.66570300

C	-1.75501900	5.47115500	-0.59657100
C	-1.40598800	5.37117900	-1.94454500
H	-1.60632600	4.16917600	-3.71863500
H	-1.41520800	6.32792100	-0.01972900
C	-3.18515600	2.13395400	-2.91935300
H	-2.84852100	2.23620300	-3.95593400
H	-2.82181200	1.17899000	-2.53194900
H	-4.28195400	2.09397100	-2.93266100
C	-2.96214600	4.69013900	1.47738900
H	-4.03161900	4.92014700	1.57428500
H	-2.77875100	3.78735300	2.06671100
H	-2.40980000	5.51627800	1.93446200
C	-0.59341000	6.44720000	-2.62774600
H	-1.20487200	7.01114000	-3.34436900
H	-0.18913100	7.16521500	-1.90679600
H	0.24593300	6.02235200	-3.19089300
H	-5.59768100	3.88615400	0.14293700
C	-4.74072200	-2.61967700	3.03247100
C	-5.75083300	-0.40805700	2.49239700
H	-7.57354200	-3.18304500	0.35195900
H	-4.91831300	-3.62513100	3.44128900
H	-3.95826100	-2.15538600	3.63563100
C	-6.02748500	-1.78332800	3.12653800
H	-6.64196700	0.22925500	2.58207500
H	-4.92870200	0.08576400	3.02049700
H	-6.30134300	-1.64238100	4.17983400

H	-7.37523100	-3.46661200	2.83014800
H	-8.09957000	-1.90252400	2.44480500
C	0.07153100	0.39228400	1.55680000
C	-0.36486700	-0.98521500	1.69650000
C	-0.93130600	1.36840700	1.96036500
C	-1.44063400	-1.30455500	2.53138400
H	0.22416700	-1.76233700	1.22667500
C	-1.99291600	1.02231100	2.82624900
H	-0.76491400	2.39698100	1.65971500
C	-2.08670300	-0.30861700	3.41657500
H	-1.68889600	-2.34771800	2.70360000
H	-2.64151500	1.79361300	3.23265100
O	-2.73760600	-0.58768600	4.43258500
H	6.30912900	-1.36107800	0.80316600

1.25-ts

Ru	-0.16447600	0.32689100	-0.10519600
O	-1.31273300	2.55151700	-0.10717400
O	1.22631700	0.77351200	-2.03386700
O	1.80457800	1.19812300	0.04618900
N	-0.71621200	-2.51490700	-0.14054000
N	1.41677100	-2.26615300	0.33072700
C	0.26360500	-1.57287000	0.06078500
C	-0.19907800	-3.88476900	-0.15996700
H	-0.09985300	-4.25043900	-1.19206500
H	-0.84951300	-4.57509000	0.38510500

C	1.16230800	-3.70772400	0.51102100
H	1.12981600	-3.95047900	1.58334400
H	1.94712000	-4.31233600	0.05089400
C	-2.10964900	-2.19431400	-0.46400700
C	-3.05182100	-2.75949900	0.63609300
H	-2.74148100	-2.39950200	1.62212000
H	-2.96471500	-3.85486700	0.65920300
C	-4.51460700	-2.36671600	0.35487000
H	-5.15447000	-2.76959600	1.15136300
C	-4.94655700	-2.95296700	-1.00328600
H	-4.89039500	-4.05044100	-0.97784400
H	-5.99260400	-2.69125800	-1.21353100
C	-4.02992800	-2.39392700	-2.10956600
H	-4.32784800	-2.80819200	-3.08176300
C	-2.56553300	-2.81210300	-1.81838400
H	-1.89579300	-2.46824000	-2.61728400
H	-2.50318200	-3.91005000	-1.78966400
C	-4.17513100	-0.85467700	-2.13793100
H	-3.58001200	-0.42870200	-2.95670200
H	-5.22485400	-0.59079100	-2.33229900
C	-3.71050100	-0.26284600	-0.77917000
H	-3.79422500	0.83030900	-0.80655800
C	-2.23252600	-0.66827700	-0.62646500
H	-1.78845600	-0.42454200	-1.59540000
C	-4.62204500	-0.82961800	0.32827300
H	-4.35206900	-0.41387800	1.30405700

H	-5.66148600	-0.53046800	0.13393100
C	2.69053800	-1.76501100	0.75633100
C	2.85292200	-1.19633000	2.03404500
C	4.14008100	-0.82741800	2.43649400
H	4.26982200	-0.38519300	3.42234600
C	5.25970500	-1.01766300	1.62083300
C	5.06649200	-1.59892400	0.36458500
H	5.92421600	-1.76203400	-0.28524400
C	3.79683000	-1.97485300	-0.08821200
C	1.68300000	-0.97852200	2.96049800
H	2.02929100	-0.70238800	3.96156300
H	1.06143600	-1.87772300	3.05300600
H	1.03457700	-0.18210500	2.57803000
C	6.63460200	-0.58640100	2.07722600
H	6.76558400	-0.73701900	3.15468000
H	6.80211600	0.48039900	1.87739000
H	7.42275100	-1.14278000	1.55869800
C	3.63370900	-2.58390400	-1.46252800
H	3.43911200	-3.66404600	-1.41733900
H	4.54354700	-2.44752300	-2.05473800
H	2.80004100	-2.12432500	-2.00275400
C	-1.52895700	0.17506600	1.20843800
H	-1.75061900	-0.69563300	1.82879100
C	-2.23421200	1.36824500	1.69505400
C	-2.99656700	1.34691400	2.87565000
H	-3.10579600	0.40023700	3.40016900

C	-3.59406600	2.49838300	3.38583000
H	-4.17060500	2.45641500	4.30532100
C	-3.44211500	3.70288600	2.70066300
H	-3.89891400	4.61197900	3.08240900
C	-2.69130500	3.76471300	1.52183500
H	-2.56830200	4.71985700	1.02621200
C	-2.08806900	2.60660800	1.02558300
C	-1.21327100	3.71239100	-0.98116200
H	-2.16232600	4.25472300	-0.90930500
C	-1.06506700	3.19055200	-2.40467300
H	-0.18749200	2.54694100	-2.50888500
H	-0.97299400	4.03616900	-3.09592200
H	-1.94995600	2.61096200	-2.68846100
C	-0.06159200	4.59634800	-0.51046600
H	-0.23801300	4.97419600	0.50157500
H	0.05929100	5.45392100	-1.18200500
H	0.86907100	4.02288100	-0.49636500
C	2.05092300	1.26262100	-1.20838500
C	3.33431800	1.95556300	-1.71179700
C	4.18124700	0.91648900	-2.47754200
H	3.59182500	0.44675500	-3.27077200
H	4.54649000	0.13603700	-1.80391000
H	5.05157300	1.40531000	-2.93331300
C	2.93523400	3.07482900	-2.69770200
H	2.34009800	2.67150000	-3.52222300
H	3.83527200	3.54322700	-3.11484400

H	2.35152500	3.86054200	-2.20553100
C	4.14441000	2.53825800	-0.54318900
H	5.05944200	3.01177200	-0.92163700
H	4.42493800	1.75787300	0.16992400
H	3.57079300	3.29344400	0.00430300

1.26

Ru	-0.17165800	0.27304600	-0.26008800
O	-1.55920600	2.36540300	-0.30125700
O	1.49368100	1.09727600	-1.75951400
O	1.59636200	1.26070800	0.43066900
N	-0.68308800	-2.52248600	0.15499700
N	1.50173200	-2.24896100	0.22336200
C	0.32433100	-1.57627900	0.03819400
C	-0.16509800	-3.89112400	0.16560300
H	-0.23173000	-4.35359800	-0.83028300
H	-0.70637100	-4.52637200	0.87296600
C	1.28971700	-3.66392600	0.57624400
H	1.44192700	-3.81418000	1.65433600
H	1.99364400	-4.30852300	0.04180400
C	-2.07177000	-2.22633900	-0.20989300
C	-3.06901600	-2.90555700	0.75922500
H	-2.85479000	-2.59251200	1.78753300
H	-2.94639800	-3.99638800	0.72006000
C	-4.51630700	-2.53626200	0.36968100
H	-5.20809500	-3.01558400	1.07457300

C	-4.80816000	-3.03125600	-1.06195100
H	-4.70405400	-4.12407600	-1.11532200
H	-5.84507800	-2.79531800	-1.33771900
C	-3.83214100	-2.35647500	-2.04681100
H	-4.02679100	-2.71454700	-3.06625300
C	-2.38351700	-2.70847600	-1.65528600
H	-1.66998600	-2.24506400	-2.34923300
H	-2.23917600	-3.79497100	-1.72003700
C	-4.01193800	-0.82770400	-1.98782300
H	-3.33926400	-0.34177700	-2.70799500
H	-5.03686400	-0.55430800	-2.27344100
C	-3.71775000	-0.33001700	-0.55904700
H	-3.84185600	0.75603500	-0.51177400
C	-2.26502600	-0.68475200	-0.14166200
H	-1.65963000	-0.30748600	-1.10698900
C	-4.69239500	-1.00630600	0.42958700
H	-4.51445200	-0.63761700	1.44604900
H	-5.72439400	-0.73697800	0.16652300
C	2.82775800	-1.74188400	0.43371300
C	3.21233900	-1.28210700	1.70619500
C	4.56478000	-0.99832700	1.92563700
H	4.87210500	-0.65041700	2.90991000
C	5.52790400	-1.15266900	0.92348500
C	5.10604600	-1.58723800	-0.33741100
H	5.83817600	-1.70356800	-1.13421300
C	3.76458700	-1.87997400	-0.60593800

C	2.19977700	-1.06905000	2.80439400
H	2.69760700	-0.84240400	3.75242300
H	1.56125900	-1.94641800	2.96039200
H	1.54457800	-0.22993600	2.54713500
C	6.97927000	-0.82115300	1.18405600
H	7.19611600	0.22652500	0.93584200
H	7.64827800	-1.44283800	0.57901400
H	7.24109600	-0.96589000	2.23777900
C	3.33095500	-2.30517400	-1.98879800
H	2.81034400	-3.27044100	-1.98377900
H	4.19399400	-2.39339300	-2.65609700
H	2.64103400	-1.56668500	-2.41344400
C	-1.69243100	-0.03768900	1.10755300
H	-1.51668600	-0.75015500	1.91631300
C	-2.28791900	1.22293300	1.63904400
C	-2.88679100	1.26663400	2.90611900
H	-2.89959100	0.35409700	3.49845200
C	-3.47328300	2.42859100	3.41248000
H	-3.93084700	2.42440100	4.39789300
C	-3.47361200	3.58484900	2.63766000
H	-3.93316200	4.49768400	3.00681300
C	-2.85992500	3.58868300	1.38053000
H	-2.84315400	4.50587300	0.80512800
C	-2.25015400	2.42761800	0.89985300
C	-1.79266500	3.37491000	-1.32243200
H	-2.84197000	3.68255600	-1.23183000

C	-1.57127900	2.70129600	-2.67186600
H	-0.55489200	2.29885300	-2.73546000
H	-1.71428100	3.43144600	-3.47686900
H	-2.28019500	1.88113500	-2.82102900
C	-0.86968900	4.57578600	-1.12496100
H	-0.94719900	4.99578400	-0.11867200
H	-1.12325000	5.36178500	-1.84615300
H	0.16828000	4.28101300	-1.29190100
C	2.07693900	1.53403600	-0.72586700
C	3.33027700	2.42306400	-0.84958700
C	4.29178100	1.79223600	-1.87647500
H	3.78948500	1.64614600	-2.83683400
H	4.65743800	0.82080400	-1.52982800
H	5.15848900	2.44766100	-2.02955900
C	2.88639200	3.80615900	-1.37503500
H	2.34298900	3.71042600	-2.32073900
H	3.76521600	4.44009400	-1.54625600
H	2.24478400	4.31744000	-0.64882000
C	4.02626600	2.59524300	0.51003300
H	4.90364200	3.24549000	0.39930400
H	4.35780800	1.63393300	0.91221400
H	3.35207300	3.04747100	1.24356000

1.27-ts

Ru	-0.23494600	0.23791500	-0.22532500
O	-1.64916000	2.29680200	-0.34349300

O	1.47348300	1.05576300	-1.58412600
O	1.46414500	1.39385900	0.58733800
N	-0.61402800	-2.52749100	0.40626200
N	1.55773800	-2.17216800	0.44291700
C	0.36109800	-1.56590500	0.19846300
C	-0.05557000	-3.87288600	0.54112800
H	-0.12143400	-4.43143000	-0.40369700
H	-0.57079900	-4.45061300	1.31456400
C	1.39796700	-3.56416400	0.90627400
H	1.57338400	-3.62726700	1.98873000
H	2.11668000	-4.22111200	0.40792500
C	-1.97044600	-2.29073100	-0.09202500
C	-3.05470000	-2.94368900	0.79730600
H	-2.95295500	-2.58395000	1.82784900
H	-2.92301200	-4.03464200	0.81727600
C	-4.45341000	-2.59932600	0.23468300
H	-5.21719300	-3.04803100	0.88322700
C	-4.59214800	-3.16042800	-1.19515200
H	-4.48211000	-4.25407400	-1.18790100
H	-5.59516700	-2.94262800	-1.58666300
C	-3.51819000	-2.52520800	-2.10071900
H	-3.60083800	-2.93193900	-3.11721000
C	-2.12310300	-2.84822400	-1.53520000
H	-1.33923500	-2.42021200	-2.17178600
H	-1.97653700	-3.93634300	-1.52255300
C	-3.69733200	-0.99552500	-2.13372800

H	-2.94887400	-0.54504600	-2.79892900
H	-4.68501900	-0.73722200	-2.53931600
C	-3.56060800	-0.42731500	-0.70799300
H	-3.69943500	0.65677100	-0.72681700
C	-2.18670600	-0.75651400	-0.08435400
H	-1.36131300	-0.41189100	-1.24170200
C	-4.64093000	-1.06873700	0.19790300
H	-4.58199400	-0.64691900	1.20727500
H	-5.63805300	-0.82669900	-0.19496500
C	2.89253800	-1.64585900	0.46533800
C	3.42885500	-1.14984700	1.66726700
C	4.79923900	-0.86990700	1.71333200
H	5.22506700	-0.49745800	2.64300800
C	5.63246700	-1.05603200	0.60546100
C	5.05781300	-1.51581900	-0.58404300
H	5.68605300	-1.65299000	-1.46193800
C	3.69396900	-1.81184800	-0.67867900
C	2.55318200	-0.87816600	2.86598900
H	3.16047800	-0.64711400	3.74672600
H	1.90452300	-1.72510200	3.11607200
H	1.90573700	-0.01938400	2.65633100
C	7.10623300	-0.72949200	0.67938100
H	7.29180500	0.32071200	0.41732900
H	7.68892100	-1.34503600	-0.01447400
H	7.50197500	-0.88700200	1.68852900
C	3.09525200	-2.27150100	-1.98618700

H	2.55047700	-3.21781000	-1.88444800
H	3.87391400	-2.41003700	-2.74264600
H	2.38422800	-1.52362700	-2.35586000
C	-1.76809000	-0.06228300	1.15489500
H	-1.52312400	-0.71506600	1.99398800
C	-2.42222000	1.19643000	1.60709200
C	-3.07782100	1.26051800	2.84478200
H	-3.07901400	0.37060800	3.47057000
C	-3.73652000	2.41273700	3.27788900
H	-4.23700800	2.42602700	4.24208900
C	-3.75372000	3.53592300	2.45594200
H	-4.27081800	4.43997200	2.76580500
C	-3.08454000	3.51912300	1.22790500
H	-3.08748800	4.41226500	0.61630800
C	-2.39876100	2.37129300	0.82186200
C	-1.87267000	3.26799700	-1.40471000
H	-2.94262300	3.51150300	-1.39108800
C	-1.52075300	2.58157300	-2.71927400
H	-0.48336200	2.23128400	-2.70230800
H	-1.64273800	3.28942800	-3.54737500
H	-2.17292400	1.72252200	-2.90070900
C	-1.04105500	4.53037400	-1.18175700
H	-1.20462900	4.96782900	-0.19364500
H	-1.30109100	5.28135600	-1.93721700
H	0.02165900	4.30215300	-1.27866300
C	1.98941300	1.59729900	-0.55791700

C	3.20746400	2.53281200	-0.70184400
C	4.15856600	1.98033700	-1.78007800
H	3.63364100	1.85244900	-2.73073100
H	4.56957200	1.00961900	-1.48675000
H	4.99525300	2.67415100	-1.93167800
C	2.69543000	3.91741700	-1.15789500
H	2.14635400	3.84266200	-2.10267400
H	3.54389600	4.59590800	-1.31085400
H	2.04094900	4.36515800	-0.40214000
C	3.93845200	2.68715200	0.64193500
H	4.78081400	3.38199900	0.53071900
H	4.32906200	1.72792300	0.99322000
H	3.26642100	3.07685100	1.41183500

1.28

Ru	0.25595400	0.14828000	0.30094300
O	1.49509900	2.14810100	0.79292100
O	-1.64278200	1.07221500	1.05915100
O	-1.05094600	1.47917500	-1.02135200
N	0.65584100	-2.45101400	-0.81458800
N	-1.52506000	-2.18523400	-0.64306900
C	-0.32812000	-1.59190400	-0.38392600
C	0.13262200	-3.77035400	-1.17534200
H	0.32037900	-4.50430600	-0.37977700
H	0.58755000	-4.14477900	-2.09733400
C	-1.36621800	-3.48126800	-1.33513600

H	-1.64976000	-3.39010300	-2.38986200
H	-2.00358000	-4.24103100	-0.87353800
C	2.00961700	-2.25343700	-0.27985000
C	3.12685100	-2.74170900	-1.23282000
H	3.03427800	-2.23486900	-2.20112100
H	3.04033000	-3.82275600	-1.41642600
C	4.50098900	-2.43395400	-0.58607600
H	5.29456200	-2.74891200	-1.27653800
C	4.63426000	-3.20386100	0.74393100
H	4.56171000	-4.28667000	0.56811000
H	5.62217800	-3.01758700	1.18707000
C	3.52138700	-2.74893500	1.70822700
H	3.59678400	-3.30645700	2.65147500
C	2.15313500	-3.02277600	1.06429000
H	1.34520700	-2.71824800	1.73772500
H	2.04633900	-4.10039100	0.87847100
C	3.63138900	-1.23833900	1.98374300
H	2.84299600	-0.93208800	2.68079200
H	4.59739300	-1.00765600	2.45483900
C	3.50383300	-0.46043000	0.66091800
H	3.61038200	0.61054100	0.85176200
C	2.18789100	-0.73808900	-0.07259300
H	0.69680400	-0.56770700	1.66755100
C	4.63651300	-0.92270400	-0.29898800
H	4.59113300	-0.34708700	-1.23080700
H	5.61687100	-0.72241200	0.15626800

C	-2.84652400	-1.75314600	-0.29301100
C	-3.73656100	-1.36311100	-1.31077700
C	-5.06964700	-1.10806900	-0.96792200
H	-5.76347700	-0.81349700	-1.75300000
C	-5.52794500	-1.20673100	0.34847800
C	-4.61110300	-1.57465000	1.33828200
H	-4.94709000	-1.65735000	2.36989600
C	-3.27388300	-1.85764000	1.04517600
C	-3.28024700	-1.19267900	-2.74161800
H	-3.98890500	-0.57123600	-3.29725100
H	-3.20866800	-2.15072900	-3.27347400
H	-2.29998100	-0.70760600	-2.78420600
C	-6.96425500	-0.89273800	0.69858700
H	-7.08396400	0.16580100	0.96548300
H	-7.30623500	-1.48340000	1.55544700
H	-7.63622900	-1.09393200	-0.14269900
C	-2.32955700	-2.27084400	2.14652500
H	-1.78197000	-3.18648400	1.89208700
H	-2.87714300	-2.45064600	3.07689500
H	-1.58303600	-1.49058100	2.33007500
C	1.77351800	0.13526200	-1.13731400
H	1.41356200	-0.31638700	-2.06275000
C	2.31604400	1.51176700	-1.33541000
C	2.94205700	1.86054000	-2.53846400
H	3.02306800	1.10317600	-3.31489100
C	3.46647400	3.13620500	-2.75645400

H	3.95185800	3.37264800	-3.69905600
C	3.35566400	4.09915200	-1.75729700
H	3.75080000	5.09992900	-1.90893100
C	2.71072500	3.79477600	-0.55440700
H	2.59720900	4.56806900	0.19590000
C	2.18853500	2.51615800	-0.34992700
C	1.61485900	2.93757300	2.01194700
H	2.59365600	3.42895600	1.97705300
C	1.58185400	1.97892200	3.19489500
H	0.64311100	1.41740600	3.20926500
H	1.66533600	2.55042600	4.12669300
H	2.40969800	1.26724100	3.14782900
C	0.49465600	3.97013500	2.07910200
H	0.49141900	4.62340500	1.20206600
H	0.61081300	4.59270500	2.97398800
H	-0.46975700	3.45668900	2.13272300
C	-1.83695800	1.68464200	-0.04440200
C	-2.98760100	2.69871500	-0.20116300
C	-3.93592800	2.64498200	1.00676400
H	-3.40975400	2.87995700	1.93711600
H	-4.37661100	1.64953100	1.11911300
H	-4.74810700	3.37162600	0.87701700
C	-2.37492400	4.11206100	-0.33248000
H	-1.87919700	4.42355100	0.59181700
H	-3.16596300	4.84098000	-0.54827300
H	-1.64305000	4.14433900	-1.14564400

C	-3.75721000	2.38653700	-1.50088400
H	-4.52787700	3.14909400	-1.67013600
H	-4.25165100	1.41282100	-1.44143200
H	-3.07896900	2.37915200	-2.35868400

1.31-ts

Ru	0.21903300	0.34316400	-0.10796100
O	1.52181500	2.33968200	0.20020600
O	-0.70313800	-0.23483600	2.57842400
O	-1.62993500	1.02550900	0.99773100
N	0.50465100	-2.38318300	-0.87640300
N	-1.61008600	-1.84888700	-1.23004200
C	-0.41761900	-1.36667300	-0.74456900
C	-0.12371800	-3.65740900	-1.21973800
H	-0.30130200	-4.27428400	-0.32580900
H	0.48310700	-4.23866700	-1.92097000
C	-1.44643100	-3.18274700	-1.83833700
H	-1.37601800	-3.09648300	-2.93264900
H	-2.28834200	-3.83898400	-1.60174000
C	1.74058700	-2.24415800	-0.09326300
C	2.95657700	-2.95479600	-0.73185300
H	3.10839000	-2.58285400	-1.75252100
H	2.78690700	-4.04002300	-0.79832500
C	4.20854800	-2.67854800	0.13834900
H	5.07811300	-3.15951100	-0.32959200
C	3.99686500	-3.25445500	1.55359400

H	3.83942000	-4.34148600	1.50383900
H	4.89632500	-3.08895800	2.16275700
C	2.77696400	-2.57287400	2.20468900
H	2.60923000	-2.99115100	3.20633200
C	1.53625700	-2.82812500	1.33160800
H	0.64716300	-2.38102400	1.78709900
H	1.35638800	-3.91041600	1.25588200
C	3.00508900	-1.05165100	2.30618000
H	2.14136000	-0.57509200	2.78473400
H	3.88291400	-0.84467500	2.93522000
C	3.22627400	-0.46610900	0.89779200
H	3.41524200	0.60946100	0.97033000
C	2.03692800	-0.72488400	-0.03217400
H	0.03492300	-0.28005100	1.61177300
C	4.45916500	-1.15902200	0.25434100
H	4.65475800	-0.72437300	-0.73315900
H	5.35358500	-0.98135800	0.86899400
C	-2.77446500	-1.06483600	-1.51016200
C	-2.75004800	-0.07024100	-2.50854100
C	-3.92236200	0.64973000	-2.76137600
H	-3.90613200	1.41792800	-3.53213200
C	-5.11105100	0.40479400	-2.06788800
C	-5.11109900	-0.60525800	-1.10175400
H	-6.02878400	-0.82287900	-0.55828000
C	-3.96213600	-1.34697200	-0.80780800
C	-1.50321600	0.22255500	-3.30966200

H	-1.73260900	0.88058400	-4.15377800
H	-1.04924100	-0.69302300	-3.70638500
H	-0.73364500	0.70649200	-2.69410200
C	-6.35364500	1.22020200	-2.34194300
H	-6.39738700	2.10683900	-1.69519700
H	-7.26423300	0.63956800	-2.15806400
H	-6.38053000	1.57390900	-3.37834100
C	-4.01654300	-2.43224400	0.24205200
H	-4.08965300	-3.43242500	-0.20709300
H	-4.89426300	-2.30671200	0.88395800
H	-3.12130400	-2.42800100	0.87127400
C	1.91783500	0.00487100	-1.28323600
H	1.73257500	-0.58816000	-2.18168000
C	2.62792100	1.27564700	-1.60182600
C	3.47427800	1.36228700	-2.71670700
H	3.64542900	0.45908400	-3.29827100
C	4.08928100	2.55716800	-3.09589400
H	4.74129800	2.58401200	-3.96460100
C	3.84648900	3.71186700	-2.35813900
H	4.29866900	4.65750200	-2.64454400
C	2.99568500	3.67028400	-1.24828200
H	2.78473000	4.59070600	-0.71696800
C	2.40193800	2.46452000	-0.87056700
C	1.35999400	3.41803800	1.16201600
H	2.23028100	4.07396200	1.07766300
C	1.37176000	2.80187600	2.55623400

H	0.57333900	2.06661300	2.67656500
H	1.23968200	3.58863500	3.30822700
H	2.32549000	2.29983000	2.74612900
C	0.08378500	4.18861300	0.83566500
H	0.12607100	4.60245600	-0.17750500
H	-0.05104700	5.01774800	1.54015300
H	-0.78419800	3.52445700	0.90204100
C	-1.65839800	0.53386500	2.14923100
C	-2.79439500	0.84143600	3.13205100
C	-3.31598200	-0.48040600	3.73512800
H	-2.51245300	-1.02907100	4.23363600
H	-3.74331400	-1.12787300	2.96159400
H	-4.10285900	-0.26801600	4.46861100
C	-2.21190100	1.72037500	4.26413400
H	-1.39683000	1.20614800	4.78249100
H	-2.99635500	1.95121300	4.99460200
H	-1.82798500	2.66961800	3.87264900
C	-3.93168300	1.58823100	2.41729900
H	-4.74173400	1.79543800	3.12684300
H	-4.33624600	0.99716600	1.58982000
H	-3.58344500	2.53893000	2.00311900

1.32

Ru	0.25750200	0.33054100	-0.09711700
O	1.55861800	2.34897200	0.15640600
O	-1.04904000	-0.26095200	2.57590200

O	-1.62030500	1.10712800	0.91424600
N	0.58293700	-2.41725700	-0.76773200
N	-1.53773600	-1.92748700	-1.15906100
C	-0.35510200	-1.40292800	-0.67656700
C	-0.02580700	-3.70837900	-1.07467000
H	-0.21903900	-4.29526300	-0.16303900
H	0.59986800	-4.31045600	-1.74135900
C	-1.33825300	-3.26915700	-1.73643400
H	-1.23865500	-3.20455400	-2.83030000
H	-2.17510100	-3.93541400	-1.50952300
C	1.79966900	-2.24140000	0.03546300
C	3.03629100	-2.95859300	-0.55486600
H	3.20386300	-2.61792300	-1.58381300
H	2.88090300	-4.04762300	-0.58992900
C	4.26823900	-2.63936300	0.32899500
H	5.15194400	-3.12649100	-0.10502600
C	4.03579600	-3.16887400	1.75909600
H	3.89183100	-4.25883600	1.74478800
H	4.92073100	-2.97110200	2.37987100
C	2.79498900	-2.48089000	2.36260800
H	2.61333700	-2.86735500	3.37485100
C	1.57685900	-2.78341000	1.47365500
H	0.67241800	-2.33278500	1.89475600
H	1.40973000	-3.86949100	1.43302700
C	3.00274600	-0.95409500	2.41525100
H	2.11971200	-0.47118600	2.85295900

H	3.86045600	-0.71331400	3.05983800
C	3.24708700	-0.41484300	0.99277300
H	3.42361800	0.66477000	1.03345800
C	2.07331800	-0.71773000	0.05545700
C	4.50031900	-1.11432600	0.39869500
H	4.70988000	-0.71061800	-0.59894300
H	5.38143900	-0.90619500	1.02334900
C	-2.71725100	-1.18035800	-1.46959000
C	-2.71065800	-0.20372700	-2.48690000
C	-3.89801900	0.48393700	-2.75829100
H	-3.89294300	1.24330600	-3.53805100
C	-5.08774700	0.21783700	-2.07336000
C	-5.06894600	-0.77018000	-1.08480500
H	-5.98410900	-0.99735400	-0.54075700
C	-3.90297400	-1.47726800	-0.76956100
C	-1.46484200	0.10378000	-3.28268100
H	-1.69146800	0.78724800	-4.10715400
H	-1.02230200	-0.80531000	-3.70760900
H	-0.68943100	0.55774600	-2.65060200
C	-6.36301200	0.95247700	-2.41831200
H	-6.16323600	1.99249900	-2.69871300
H	-7.06343800	0.95763200	-1.57628400
H	-6.87761400	0.48179500	-3.26711000
C	-3.93370200	-2.53783700	0.30667300
H	-3.92089900	-3.55112900	-0.11731400
H	-4.84594000	-2.45597400	0.90631600

H	-3.06912600	-2.46081900	0.97367900
C	1.97038600	-0.04136800	-1.23184700
H	1.81715600	-0.67471700	-2.10865700
C	2.68831800	1.21346800	-1.58754100
C	3.55778600	1.25522300	-2.68737000
H	3.73136100	0.33104100	-3.23417800
C	4.19336800	2.43033500	-3.09365200
H	4.86201600	2.42137800	-3.95008600
C	3.95268000	3.61053400	-2.39719600
H	4.42428400	4.54065900	-2.70250900
C	3.07927200	3.61433500	-1.30389800
H	2.87503500	4.55318200	-0.80339300
C	2.45986800	2.42891900	-0.90317400
C	1.34730800	3.49516800	1.01974600
H	2.26385100	4.09273000	1.00862000
C	1.14642200	2.97547300	2.43773600
H	0.25859000	2.34317200	2.50387200
H	1.02293300	3.82078600	3.12484400
H	2.01128000	2.38856500	2.76076900
C	0.16970000	4.31566100	0.49869300
H	0.34810300	4.65070300	-0.52810700
H	0.01197000	5.20014400	1.12704000
H	-0.74204500	3.70920100	0.51011800
C	-1.85645500	0.63539600	2.03573100
C	-3.03995800	1.06748200	2.89928900
C	-3.75693400	-0.17815900	3.46268200

H	-3.07507800	-0.79660400	4.05269700
H	-4.17140500	-0.79478200	2.65876800
H	-4.58518800	0.13737600	4.10769200
C	-2.47966600	1.90646700	4.07397800
H	-1.77967200	1.32305100	4.67996500
H	-3.30564200	2.23151600	4.71711700
H	-1.96221000	2.80192300	3.71184100
C	-4.01343800	1.91316700	2.06248100
H	-4.86251100	2.21921200	2.68459200
H	-4.39534400	1.34760000	1.20699100
H	-3.52778400	2.81358300	1.67523500
H	-0.29272100	-0.38797000	1.86394000

1.33

C	0.73454100	-1.33134700	0.97116600
C	0.09207400	-2.51518500	2.91032200
C	1.52509200	-1.99276000	3.09166600
C	-1.53378400	-2.24770700	0.92892800
C	-1.45073500	-3.70964400	0.41194900
C	-2.73515500	-4.09473000	-0.34441700
C	-3.95287500	-3.94160700	0.58628100
C	-4.04523000	-2.47771500	1.05975300
C	-2.77145500	-2.12193600	1.85648200
C	-4.17828900	-1.54346700	-0.16201500
C	-2.93224100	-1.69757500	-1.08491000
C	-1.72697000	-1.25958800	-0.23653600

C	-2.88069700	-3.16271500	-1.55982100
C	3.15389400	-0.88386000	1.55251500
C	4.16582700	-1.76105200	1.11906400
C	3.89759000	-3.22714600	0.86489200
C	-1.50197400	0.12694100	-0.00562800
C	0.29692400	-2.35913500	-2.93071100
C	1.34364000	-2.37723900	-1.90711300
C	2.31598100	-1.33944400	-1.83962500
C	2.16770500	-0.12876400	-2.60472200
C	0.81115100	0.07776300	-3.14193700
C	-0.09069000	-0.96571900	-3.25717200
H	0.05894300	-3.60922000	2.83486500
H	2.24183500	-2.78268500	3.33445000
H	-1.30638500	-4.38660800	1.26544200
H	-0.58236300	-3.81326600	-0.24673100
H	-2.65178800	-5.13532400	-0.68316400
H	-3.86384300	-4.61433600	1.45178300
H	-4.87069300	-4.22501100	0.05392400
H	-4.91855600	-2.35260800	1.71411000
H	-2.67530100	-2.80435500	2.71341900
H	-5.08148800	-1.80244200	-0.73149000
H	-4.28693600	-0.50479800	0.16560300
H	-3.04304400	-1.03334200	-1.94553800
H	-3.81543500	-3.38946600	-2.09241900
H	-2.06463700	-3.32572900	-2.26498800
H	3.93965300	-3.80642500	1.79798500

H	2.91181900	-3.39612600	0.42491100
H	4.65005000	-3.64939300	0.19191100
H	1.54165900	-3.33425300	-1.43263500
H	3.23776100	-1.46251100	-1.28535400
H	0.56730400	1.07206900	-3.50580100
H	-1.05026600	-0.82469000	-3.74704700
N	-0.30167200	-1.89278100	1.63987200
N	1.83123900	-1.40155700	1.77206600
O	0.96648600	1.83315900	-0.41814100
O	-0.28781900	-3.35173900	-3.36985600
O	3.04787700	0.77475300	-2.64329900
Ru	0.38608100	-0.61839800	-0.89958600
C	5.45979700	-1.25543100	0.95462800
H	6.24214700	-1.92422300	0.60182500
C	3.44724200	0.44949100	1.89374200
C	5.77306900	0.07802300	1.23098700
C	4.75647900	0.90641300	1.71668000
H	4.98760700	1.93908400	1.96951800
C	2.39097300	1.36529900	2.46192300
H	1.58086100	1.52668000	1.74633500
H	1.95171600	0.95886200	3.38181900
H	2.82467700	2.33917500	2.71041000
C	7.16628900	0.61380800	1.00015800
H	7.41998000	1.39754900	1.72222000
H	7.91944500	-0.17750100	1.07717500
H	7.25451300	1.05336900	-0.00198800

H	1.59156300	-1.22422600	3.87106100
H	-0.57167400	-2.21113500	3.72462100
H	-1.16005000	0.39080500	0.99217700
C	-2.30761000	1.23311700	-0.60822400
C	-3.11677600	2.02648800	0.25130700
C	-2.33425400	1.54442600	-1.97172200
C	-3.89358900	3.07241300	-0.26117100
C	-3.11766900	2.57716300	-2.49312800
H	-1.70822000	0.96416400	-2.63609300
C	-3.89619200	3.34362100	-1.63167500
H	-4.50477600	3.68058600	0.39481100
H	-3.10743200	2.78151500	-3.56002000
H	-4.50673800	4.15785000	-2.01272200
O	-3.09915800	1.67223100	1.57853100
C	-3.89780100	2.37739500	2.54584100
H	-4.88068800	2.59016300	2.10544700
C	-4.08585900	1.41488400	3.71461500
H	-3.11623800	1.14613900	4.14834100
H	-4.69594500	1.88068200	4.49617200
H	-4.58442600	0.49810800	3.38527700
C	-3.21864700	3.67968400	2.97335600
H	-3.83994200	4.21021400	3.70418100
H	-2.24957000	3.46263600	3.43585300
H	-3.04643100	4.34541200	2.12325400
C	1.30704000	2.90452100	-0.93271200
H	-2.82721800	-1.09881600	2.24381600

O	2.05204800	3.01661500	-2.01287200
H	2.43999400	2.11074300	-2.32548600
C	0.89341500	4.27754200	-0.37290600
C	0.05328300	4.11873000	0.90069300
H	-0.27742300	5.10533800	1.24713500
H	-0.82959700	3.50199700	0.71934300
H	0.62952600	3.65481100	1.70711800
C	2.17230200	5.08918700	-0.06583800
H	2.77645300	5.23038800	-0.96563300
H	1.89905500	6.07459000	0.33035600
H	2.79174300	4.58551700	0.68624100
C	0.06851600	5.00826600	-1.45874100
H	-0.84871700	4.45859600	-1.69751700
H	-0.21772000	6.00256400	-1.09507300
H	0.64923000	5.13015900	-2.37722500

1.34

C	-0.86509400	-0.58414500	-1.06215600
C	-0.46831300	-1.02689000	-3.33371400
C	-1.81570500	-0.30258600	-3.18755300
C	1.34595000	-1.48366800	-1.52666500
C	1.21597700	-3.02865300	-1.46836600
C	2.52688300	-3.66633900	-0.97436000
C	3.68337600	-3.27229000	-1.91370500
C	3.82219200	-1.73612000	-1.93584200
C	2.51541500	-1.11492600	-2.47562100

C	4.09533800	-1.22181900	-0.50751500
C	2.91705700	-1.61772300	0.43144900
C	1.67892100	-0.90935300	-0.12937800
C	2.80587200	-3.15524000	0.44933900
C	-3.22116300	0.23343800	-1.15767300
C	-4.38712200	-0.55453700	-1.17746900
C	-4.38594700	-1.96052900	-1.73218100
C	1.46333200	0.48134800	0.10102100
C	-0.30589700	-2.70824600	2.31181800
C	-1.52793100	-2.35431800	1.58400800
C	-2.25481600	-1.18522100	1.86932200
C	-1.81450300	-0.21539000	2.88558000
C	-0.38329600	-0.36933100	3.23178800
C	0.32527300	-1.52410300	2.93936400
H	-0.59974300	-2.08482300	-3.59938400
H	-2.63447600	-0.81054200	-3.70237500
H	0.96842100	-3.40684400	-2.47048900
H	0.39267000	-3.29436800	-0.79647200
H	2.41178600	-4.75760200	-0.96081000
H	3.49959500	-3.64997400	-2.92994300
H	4.62051800	-3.72889400	-1.56801400
H	4.65081900	-1.44695900	-2.59574100
H	2.32014700	-1.49656900	-3.48816500
H	5.02585400	-1.66229000	-0.12414800
H	4.22770300	-0.13332100	-0.50913000
H	3.13681200	-1.25838300	1.43733000

H	3.75500800	-3.57159800	0.81593300
H	2.02156900	-3.48613100	1.13535900
H	-4.45457100	-1.97038300	-2.82894000
H	-3.47298500	-2.49988400	-1.46037800
H	-5.24316400	-2.52532600	-1.35371100
H	-1.93635100	-3.11218500	0.92090600
H	-3.22710600	-1.01427800	1.41973500
H	0.07863900	0.45170000	3.77254900
H	1.35039200	-1.65269600	3.27567700
N	0.08125300	-0.89190500	-1.97877800
N	-2.01885500	-0.30699300	-1.72285100
O	0.21316300	-3.83039200	2.29218300
O	-2.48514800	0.76328700	3.23484300
Ru	-0.32891900	-0.53293100	0.88095900
C	-5.56624100	-0.01233800	-0.65415000
H	-6.46879400	-0.61979700	-0.65893600
C	-3.23544100	1.54034800	-0.63195700
C	-5.61213800	1.27583700	-0.11534200
C	-4.43664700	2.03411000	-0.11814300
H	-4.45162400	3.03895800	0.29806800
C	-1.99247200	2.39827600	-0.59228600
H	-1.31637500	2.08704000	0.21526700
H	-1.42005800	2.34591200	-1.52500900
H	-2.25433500	3.44502400	-0.40992800
C	-6.88510900	1.83087800	0.47893700
H	-7.75760400	1.23946900	0.18346800

H	-6.83845400	1.82933900	1.57540900
H	-7.05513700	2.86713700	0.16474800
H	-1.76902300	0.73252500	-3.55206000
H	0.17983700	-0.56251500	-4.08124400
H	1.04983400	1.02064400	-0.74631100
C	2.24464100	1.40346400	0.97009800
C	2.59362400	2.67911500	0.44160300
C	2.65703800	1.12896800	2.28322600
C	3.31628900	3.59982300	1.20868700
C	3.38686900	2.03914700	3.04778000
H	2.37726700	0.18229300	2.72578600
C	3.71560500	3.27864900	2.50743100
H	3.57594900	4.57077700	0.80421800
H	3.68149300	1.78154200	4.06106600
H	4.27530600	4.00606000	3.08910100
O	2.20320300	2.91471200	-0.85382000
C	2.41394900	4.19406700	-1.47413600
H	3.42985800	4.53968700	-1.24146600
C	2.31814300	3.94272500	-2.97585900
H	1.32335000	3.56486600	-3.23747100
H	2.49110400	4.87157300	-3.52997100
H	3.06238800	3.20468000	-3.29093500
C	1.38512100	5.21533700	-0.98537600
H	1.56433600	6.19095100	-1.45154000
H	0.37415800	4.88636600	-1.25082400
H	1.42742600	5.34161900	0.10019500

H	2.59928700	-0.02300400	-2.53989700

1.29-ts

Ru	-0.13150000	0.49175100	-0.33833200
O	-0.08717500	2.75528400	-0.40406300
O	-0.56134900	-0.75846500	2.60750300
O	-1.52520900	0.71175200	1.18264700
N	0.94875800	-2.28916200	-0.34808300
N	-1.22119600	-2.22415200	-0.68710500
C	-0.11374300	-1.45629600	-0.41874300
C	0.55398000	-3.70735100	-0.44287300
H	0.57712000	-4.18136200	0.54559600
H	1.21355200	-4.27051200	-1.10998000
C	-0.87641200	-3.61937100	-0.97914600
H	-0.92962300	-3.81407800	-2.06051600
H	-1.55593900	-4.31356400	-0.47607400
C	2.35607500	-1.90838100	-0.13803800
C	3.13532800	-2.07683200	-1.47047200
H	2.74821600	-1.36370600	-2.20893000
H	2.95490900	-3.08298200	-1.87195000
C	4.64696800	-1.86777400	-1.25199400
H	5.17055100	-1.99381900	-2.20878100
C	5.18483600	-2.88402500	-0.22609200
H	5.03967900	-3.90948900	-0.59405200
H	6.26595900	-2.74387400	-0.09043100
C	4.45101300	-2.69278400	1.11575400

H	4.81854200	-3.42253300	1.84922900
C	2.94678100	-2.90349800	0.90540300
H	2.39882500	-2.79350300	1.84988400
H	2.78597500	-3.92941800	0.55617500
C	4.66228800	-1.26679000	1.63318400
H	4.15971700	-1.13467800	2.60047300
H	5.73045800	-1.06661100	1.79652500
C	4.10683200	-0.25892900	0.60755000
H	4.27901700	0.73278000	1.02671400
C	2.56457300	-0.44691600	0.42397100
H	2.13465000	-0.46383800	1.43632900
C	4.86594600	-0.43917200	-0.72610000
H	4.51685900	0.27138500	-1.48445200
H	5.93765800	-0.24691200	-0.57436100
C	-2.53895800	-1.73892900	-0.97575300
C	-2.82999900	-1.16378800	-2.22940600
C	-4.13917500	-0.73144400	-2.47460800
H	-4.36909900	-0.28412100	-3.43984800
C	-5.15760700	-0.87610600	-1.52834000
C	-4.84591500	-1.49453800	-0.31344700
H	-5.62984800	-1.63648200	0.42785400
C	-3.55289300	-1.93513800	-0.01718300
C	-1.78031800	-1.03482200	-3.31024600
H	-2.22105400	-0.62822000	-4.22620300
H	-1.33575200	-2.00669500	-3.55869900
H	-0.95916300	-0.37971800	-2.99641100

C	-6.55524300	-0.37214600	-1.80560700
H	-6.70418200	0.63358100	-1.39011800
H	-7.31335200	-1.02211100	-1.35468000
H	-6.75484000	-0.31319400	-2.88094200
C	-3.26610000	-2.63085000	1.29228000
H	-3.17261500	-3.71726300	1.15231800
H	-4.08417900	-2.47069000	2.00175200
H	-2.33608900	-2.27722300	1.74523100
C	1.72605800	0.70806800	-0.19989900
C	2.20973900	2.14490400	-0.29478400
C	3.54343600	2.60462200	-0.35582500
H	4.35535600	1.90247500	-0.40017800
C	3.88671200	3.95492500	-0.40264900
H	4.93449000	4.23753300	-0.44804200
C	2.89049000	4.92454000	-0.39264000
H	3.13851500	5.98217300	-0.40685900
C	1.55597000	4.52747200	-0.38651600
H	0.77658700	5.27918700	-0.40084900
C	1.22452100	3.17065400	-0.36933400
C	-1.10815800	3.60069100	-1.03343200
H	-1.09114600	4.56224100	-0.50942600
C	-2.45499300	2.93879000	-0.78772700
H	-2.55088300	2.01259600	-1.36440100
H	-3.24896300	3.62532700	-1.10397900
H	-2.58156600	2.68971300	0.26659000
C	-0.80995100	3.78737800	-2.51898500

H	0.15387000	4.27398300	-2.69200700
H	-1.59180500	4.40674200	-2.97280300
H	-0.80289100	2.81319100	-3.01885400
C	-1.35727100	0.14982600	2.34860400
C	-2.23375300	0.77001200	3.47489600
C	-2.21909900	-0.14549100	4.70928800
H	-1.19676500	-0.32216300	5.05311000
H	-2.66085400	-1.12212100	4.48214700
H	-2.79454400	0.30794400	5.52686100
C	-1.60669100	2.13595500	3.83615400
H	-0.57804300	2.01154500	4.19526400
H	-2.18490600	2.62702900	4.62971200
H	-1.58423500	2.79801600	2.96435500
C	-3.68213000	0.98293400	2.99655100
H	-4.28389300	1.43324900	3.79703700
H	-4.15291600	0.03281300	2.71846700
H	-3.72100000	1.63974000	2.12386800
H	1.08374100	0.42881200	-1.62022300

1.30

Ru	-0.23341300	0.54616100	-0.10635600
O	0.02041100	2.90410500	-0.08157100
O	0.17208200	0.42290700	2.17050200
O	-1.95115200	0.59928600	1.59216500
N	0.77995400	-2.22423400	-0.15637900
N	-1.38199200	-2.16369600	-0.58474400

C	-0.27878100	-1.39183900	-0.32390800
C	0.35583600	-3.63551900	-0.09348500
H	0.32252100	-3.97407500	0.95013100
H	1.03112300	-4.29540700	-0.64307700
C	-1.04253000	-3.58818400	-0.71014100
H	-1.04325600	-3.89467300	-1.76560700
H	-1.76186700	-4.21463200	-0.17480800
C	2.21219700	-1.87305100	-0.06580100
C	2.90716400	-2.37224200	-1.36347800
H	2.51296800	-1.80637600	-2.21781700
H	2.65569300	-3.42609900	-1.53506900
C	4.43658900	-2.22021500	-1.27576700
H	4.89111300	-2.61438700	-2.19432500
C	4.98953300	-2.97814900	-0.05425300
H	4.77603200	-4.05296200	-0.14065600
H	6.08205200	-2.87218100	-0.01308300
C	4.34913800	-2.41036200	1.22695700
H	4.74070400	-2.94061800	2.10501200
C	2.82605300	-2.62139600	1.15240000
H	2.33275300	-2.26972900	2.06727000
H	2.62587900	-3.69686700	1.06927900
C	4.65904100	-0.90735200	1.34274100
H	4.24075900	-0.50294100	2.27361600
H	5.74558100	-0.74858300	1.38391200
C	4.06579800	-0.16066500	0.12611100
H	4.29002700	0.90521500	0.23001000

C	2.50815400	-0.33886900	0.15932600
H	2.23730400	-0.16082500	1.21096200
C	4.74479400	-0.72397800	-1.14332300
H	4.40162200	-0.22714500	-2.05622100
H	5.82858000	-0.55422300	-1.07860100
C	-2.64718500	-1.71049100	-1.09898900
C	-2.77149900	-1.37781800	-2.46347000
C	-4.02919800	-0.99395300	-2.94006700
H	-4.12916500	-0.72684900	-3.99026300
C	-5.15662300	-0.95514600	-2.11449200
C	-5.00768400	-1.33760200	-0.77869500
H	-5.87692400	-1.33856600	-0.12411000
C	-3.77059500	-1.72241400	-0.25189800
C	-1.59903300	-1.44265900	-3.41408900
H	-1.91035900	-1.15959000	-4.42449900
H	-1.17568300	-2.45347300	-3.47323800
H	-0.79912400	-0.76597600	-3.09810000
C	-6.49632300	-0.50394400	-2.64902600
H	-6.63835500	0.57531500	-2.50276600
H	-7.32344000	-1.01050400	-2.13957300
H	-6.58735500	-0.70043400	-3.72284600
C	-3.65714600	-2.13539300	1.19425400
H	-3.22423100	-3.13739900	1.30439300
H	-4.64271900	-2.14513600	1.67058900
H	-3.01794100	-1.42900500	1.73030900
C	1.57704600	0.69933400	-0.49605000

C	2.03583200	2.03015600	-0.97437500
C	3.22366800	2.26982100	-1.69210500
H	3.88605900	1.44660300	-1.89905700
C	3.56306300	3.52334900	-2.19757400
H	4.48367900	3.64701900	-2.76064700
C	2.71345600	4.60116900	-1.97883700
H	2.95813200	5.58907200	-2.35923500
C	1.52260600	4.41587100	-1.27411400
H	0.86976100	5.26658100	-1.13245800
C	1.18002800	3.15328000	-0.78518500
C	-1.03919200	3.91582700	-0.05803700
H	-0.54935000	4.88795700	0.04076500
C	-1.87744300	3.69393400	1.19000200
H	-2.36808700	2.71907500	1.17938400
H	-2.63683200	4.48265600	1.24735300
H	-1.25117900	3.75496900	2.08625600
C	-1.84083400	3.84987900	-1.35404000
H	-1.20034600	4.00694100	-2.22774400
H	-2.61596200	4.62492100	-1.35130300
H	-2.31841500	2.87013000	-1.45007800
C	-1.05500700	0.50836900	2.48626900
C	-1.42963900	0.48178300	3.98334400
C	-1.09634300	-0.92725300	4.52354100
H	-0.03904700	-1.16102500	4.36487600
H	-1.69683600	-1.69637900	4.02257100
H	-1.30830000	-0.98418000	5.59867100

C	-0.56887000	1.52516800	4.72540200
H	0.49536200	1.33817000	4.55918700
H	-0.77060200	1.48803500	5.80337100
H	-0.79236300	2.54137000	4.37810100
C	-2.92138100	0.78615500	4.18967100
H	-3.16424400	0.76839400	5.25984600
H	-3.55503700	0.05337500	3.68174800
H	-3.18234400	1.77414000	3.79658100
H	-0.78275600	0.74070600	-1.61315700

1.35

Ru	-0.09902000	0.38607000	0.39057000
O	1.21417100	2.27553100	0.86195000
N	-0.08311000	-2.16594700	-0.86469200
N	-2.20592100	-1.58080100	-0.59252400
C	-0.91055900	-1.17504400	-0.35754800
C	-0.83948100	-3.37045800	-1.21145800
H	-0.82260700	-4.11163500	-0.39800600
H	-0.45528000	-3.85106200	-2.11718200
C	-2.25869800	-2.80613300	-1.40332200
H	-2.46179300	-2.57046700	-2.45881800
H	-3.03878100	-3.48952100	-1.05214700
C	1.26432300	-2.17914500	-0.27029800
C	2.33415300	-2.80741500	-1.18993700
H	2.35317900	-2.27474300	-2.14897100
H	2.09790400	-3.86065400	-1.40583100

C	3.71235900	-2.71567600	-0.48986500
H	4.47802800	-3.14162700	-1.15249500
C	3.67924000	-3.50480200	0.83538700
H	3.45462900	-4.56396000	0.64341600
H	4.66688500	-3.46935700	1.31610300
C	2.61012400	-2.89928700	1.76756000
H	2.57166600	-3.47081700	2.70536900
C	1.24168800	-2.96524200	1.07053100
H	0.46402300	-2.53357500	1.71195800
H	0.97719000	-4.01522100	0.88101600
C	2.93606600	-1.42384200	2.06586400
H	2.17561300	-1.00131000	2.73579000
H	3.90639600	-1.34552100	2.57749400
C	2.97079700	-0.62986400	0.74658300
H	3.22925900	0.41349100	0.95532500
C	1.63031700	-0.69765700	0.00302700
C	4.05573300	-1.24284900	-0.18102800
H	4.12249000	-0.66149100	-1.10851700
H	5.04119300	-1.18856100	0.30469100
C	-3.34205400	-0.72932700	-0.41857800
C	-3.58983300	0.32826900	-1.31817400
C	-4.71464400	1.13272500	-1.10689100
H	-4.90788100	1.95257000	-1.79632500
C	-5.59704000	0.91223300	-0.04390700
C	-5.32593600	-0.14460200	0.83022000
H	-5.99520200	-0.32728700	1.66893100

C	-4.21111000	-0.97313400	0.66232800
C	-2.66393400	0.60196000	-2.48021600
H	-3.03619800	1.43530200	-3.08440300
H	-2.56926500	-0.27174600	-3.13662200
H	-1.65443900	0.84545600	-2.12508200
C	-6.82409400	1.77632000	0.13736900
H	-6.64270700	2.80538700	-0.19170400
H	-7.14256100	1.80634700	1.18495200
H	-7.67064600	1.39365800	-0.44887700
C	-3.94684300	-2.10126100	1.63255000
H	-4.12418200	-3.08260100	1.17267200
H	-4.60443200	-2.02560600	2.50428400
H	-2.90824700	-2.09637600	1.97865700
C	1.34078100	0.27213400	-1.07407900
H	1.04354000	-0.13206700	-2.04586200
C	2.09493500	1.55213800	-1.21483600
C	2.86117000	1.82469600	-2.35686200
H	2.90028500	1.06779300	-3.13701200
C	3.56780800	3.01960400	-2.51321600
H	4.15181700	3.19412900	-3.41269900
C	3.51712900	3.97997400	-1.50738600
H	4.06064800	4.91555300	-1.60712700
C	2.74676700	3.75550300	-0.36065600
H	2.69841000	4.52656500	0.39918900
C	2.03596300	2.56228600	-0.22678800
C	1.01502200	3.24001600	1.92186700

H	1.98400600	3.70418500	2.13936500
C	0.57026700	2.44721600	3.14495400
H	-0.38883600	1.94863000	2.95623700
H	0.44267600	3.11865500	4.00137500
H	1.30944600	1.68277300	3.40017400
C	-0.00201800	4.29799100	1.49579200
H	0.31616200	4.81757900	0.58761100
H	-0.13369800	5.04119300	2.29047500
H	-0.97236200	3.82788400	1.29850900

PivOH

C	-0.57274900	-0.01017700	0.00005100
C	-0.97332200	-0.80541000	-1.26342000
H	-0.68832900	-0.26934800	-2.17614900
H	-0.49885900	-1.79065500	-1.28143000
H	-2.06043000	-0.94440000	-1.28118900
C	-1.25107300	1.36823500	-0.00075700
H	-2.34024400	1.24637700	-0.00008500
H	-0.96700400	1.95048100	0.88111000
H	-0.96812500	1.94887300	-0.88405300
C	-0.97345000	-0.80427100	1.26412100
H	-0.49930500	-1.78969500	1.28283600
H	-0.68831200	-0.26795300	2.17670000
H	-2.06061400	-0.94294300	1.28215800
C	0.94424800	0.18600300	0.00001400
O	1.61696800	-0.99611700	-0.00007700

H	2.56396300	-0.76039800	-0.00068500
O	1.52869900	1.24779100	0.00016800

Benzoquinone

C	1.44562300	0.00003800	0.00010500
C	0.67176100	1.26929100	0.00022100
C	-0.67167900	1.26921900	-0.00022500
C	-1.44567300	-0.00004200	-0.00043900
C	-0.67171300	-1.26927300	-0.00010000
C	0.67167500	-1.26918000	0.00007000
H	1.25975500	2.18288300	0.00044400
H	-1.25986900	2.18270000	-0.00042400
H	-1.25963700	-2.18291300	-0.00001500
H	1.25980900	-2.18268300	0.00012600
O	2.67075100	-0.00007000	-0.00006800
O	-2.67075300	0.00003200	0.00032800

Appendix C

THE CARTESIAN COORDINATES (Å), SCF ENERGIES, ENTHALPIES AT 298K, AND GIBBS FREE ENERGIES AT 298K FOR OPTIMIZED STRUCTURES (CHAPTER 3)

3.6

B3LYP SCF energy:	-1378.80943708 a.u.
B3LYP enthalpy:	-1378.265763 a.u.
B3LYP free energy:	-1378.354118 a.u.
M06 SCF energy in solution:	-1379.29385334 a.u.
M06 enthalpy in solution:	-1378.750179 a.u.
M06 free energy in solution:	-1378.838534 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.221418	1.045699	0.243937
O	1.352359	2.324036	-0.558184
O	-0.297726	3.317514	0.459632
N	-0.964268	-1.605015	-0.626983
N	1.209359	-1.639479	-0.285630
C	0.103342	-0.857736	-0.238986
C	-0.628955	-3.025515	-0.772929
H	-1.081353	-3.459521	-1.669284
H	-0.973574	-3.598781	0.098740
C	0.908273	-2.973131	-0.848922
H	1.395351	-3.763558	-0.271661
H	1.271207	-3.032358	-1.883623
C	-2.299978	-1.060345	-0.353653
C	-2.811052	-1.536223	1.029452
H	-2.059455	-1.296431	1.788749
H	-2.942951	-2.627595	1.021662
C	-4.146559	-0.845916	1.366419
H	-4.495606	-1.195140	2.347247
C	-5.188073	-1.202974	0.287028
H	-5.364972	-2.287919	0.275121
H	-6.150209	-0.725176	0.516083
C	-4.681976	-0.727697	-1.090604
H	-5.420086	-0.980600	-1.862935
C	-3.346595	-1.439324	-1.425774
H	-2.984694	-1.135476	-2.417004
H	-3.505234	-2.527734	-1.454619
C	-4.481277	0.803561	-1.046853
H	-4.159731	1.175224	-2.029193
H	-5.437886	1.293826	-0.817999
C	-3.422948	1.164754	0.030301
H	-3.272824	2.251021	0.048468
C	-2.112089	0.471115	-0.364329
H	-1.882899	0.761426	-1.416989
C	-3.922354	0.679703	1.405035
H	-3.190265	0.933413	2.181311
H	-4.859681	1.191777	1.662043
C	2.569791	-1.196367	-0.148358
C	3.264708	-1.513879	1.034303
C	4.600969	-1.121890	1.146629
H	5.142644	-1.361405	2.059284
C	5.256611	-0.430354	0.122587
C	4.541980	-0.145244	-1.043254
H	5.036735	0.384207	-1.854850
C	3.202172	-0.514957	-1.204319
C	2.593690	-2.249893	2.170345
H	3.295208	-2.406695	2.995123
H	2.218278	-3.234268	1.864158

H	1.737099	-1.688086	2.558674
C	6.691343	0.016130	0.281250
H	6.742784	1.044401	0.662781
H	7.225092	-0.001118	-0.675145
H	7.235187	-0.621390	0.986354
C	2.478040	-0.150627	-2.479327
H	1.726716	-0.893901	-2.763664
H	3.186240	-0.051666	-3.308237
H	1.965875	0.811699	-2.363930
C	-0.261883	0.694957	2.031838
H	0.029991	-0.230924	2.539756
O	1.325983	4.517681	-0.402945
N	0.806457	3.449497	-0.168269
H	-0.533445	1.524256	2.701229

3.8

B3LYP SCF energy:	-1536.03762970 a.u.
B3LYP enthalpy:	-1535.374117 a.u.
B3LYP free energy:	-1535.472050 a.u.
M06 SCF energy in solution:	-1536.45146189 a.u.
M06 enthalpy in solution:	-1535.787949 a.u.
M06 free energy in solution:	-1535.885882 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.278681	0.951366	-0.094649
O	1.099384	1.939049	-1.528488
O	-0.556305	3.113991	-0.747766
N	-0.989926	-1.842127	-0.218439
N	1.193625	-1.803733	0.010867
C	0.079712	-1.012280	-0.051054
C	-0.656005	-3.262560	-0.111839
H	-1.127747	-3.852557	-0.904004
H	-0.980858	-3.668723	0.855868
C	0.874947	-3.227319	-0.232585
H	1.374886	-3.871021	0.496349
H	1.217531	-3.518747	-1.234312
C	-2.342501	-1.297370	-0.224589
C	-3.128535	-1.694188	1.051329
H	-2.554749	-1.422300	1.942791
H	-3.254641	-2.785933	1.072526
C	-4.513810	-1.014027	1.054664
H	-5.051187	-1.299792	1.968226
C	-5.309046	-1.477064	-0.182354
H	-5.461386	-2.565136	-0.152180
H	-6.305176	-1.015011	-0.184896
C	-4.539826	-1.082115	-1.459105
H	-5.100318	-1.407243	-2.345203
C	-3.159862	-1.780901	-1.456679
H	-2.603129	-1.551377	-2.374326
H	-3.296402	-2.871489	-1.421153
C	-4.363481	0.452100	-1.494333
H	-3.856170	0.758905	-2.418593
H	-5.347342	0.941010	-1.493855
C	-3.546643	0.917671	-0.253111

H	-3.410668	2.004240	-0.291311
C	-2.182372	0.224514	-0.357769
H	-1.801206	0.432766	-1.404672
C	-4.337852	0.517299	1.011262
H	-3.837781	0.874935	1.915494
H	-5.323662	1.001766	0.985035
C	2.563261	-1.396707	-0.151354
C	3.441334	-1.530015	0.943834
C	4.784201	-1.188079	0.769064
H	5.462567	-1.280026	1.614835
C	5.277265	-0.732600	-0.458773
C	4.390076	-0.649843	-1.533422
H	4.758500	-0.322232	-2.503373
C	3.034996	-0.981990	-1.410992
C	2.961613	-2.039262	2.283262
H	3.725597	-1.883740	3.050914
H	2.743667	-3.115523	2.255546
H	2.046172	-1.534183	2.604226
C	6.725921	-0.331403	-0.612090
H	6.871870	0.725394	-0.352076
H	7.071346	-0.462460	-1.642982
H	7.377546	-0.919874	0.043023
C	2.141935	-0.887458	-2.626661
H	1.318521	-1.607384	-2.597426
H	2.720699	-1.072629	-3.537722
H	1.703490	0.112780	-2.707152
C	-1.089136	1.108761	1.896867
C	1.137457	1.366942	1.476790
C	0.233377	0.945504	2.627711
H	-1.463244	2.140962	1.909947
H	-1.874242	0.437962	2.236703
H	0.383143	-0.127165	2.812293
H	1.985989	0.702530	1.299904
C	1.597186	2.818366	1.466081
H	2.250672	3.008125	2.332144
H	2.181783	3.042355	0.568995
H	0.766971	3.530150	1.519260
C	0.354969	1.676760	3.974012
H	-0.391355	1.297256	4.683586
H	1.346432	1.532298	4.423041
H	0.189754	2.754294	3.864711
N	0.450288	3.068326	-1.535900
O	0.788558	3.994837	-2.242538

3.9

B3LYP SCF energy:	-1536.03033809 a.u.
B3LYP enthalpy:	-1535.366408 a.u.
B3LYP free energy:	-1535.464862 a.u.
M06 SCF energy in solution:	-1536.44322417 a.u.
M06 enthalpy in solution:	-1535.779294 a.u.
M06 free energy in solution:	-1535.877748 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.412524	0.823417	0.007527

O	0.065171	1.658132	-2.020255
O	1.259606	2.860394	-0.656685
N	0.771300	-1.962358	0.102984
N	-1.399606	-1.745059	-0.164076
C	-0.244230	-1.052741	0.022711
C	0.359108	-3.301202	-0.327614
H	0.793524	-4.081761	0.302843
H	0.658552	-3.491327	-1.368713
C	-1.169529	-3.205923	-0.181571
H	-1.711907	-3.668094	-1.011191
H	-1.516864	-3.661038	0.754027
C	2.139210	-1.426428	0.019764
C	2.554471	-1.149450	-1.452823
H	1.820161	-0.491666	-1.939740
H	2.556813	-2.092703	-2.018004
C	3.952449	-0.499083	-1.495829
H	4.230741	-0.315074	-2.541447
C	4.977182	-1.448492	-0.843151
H	5.030439	-2.394564	-1.400292
H	5.979094	-1.000171	-0.877899
C	4.570860	-1.714009	0.621144
H	5.297528	-2.390034	1.090492
C	3.177213	-2.383007	0.649363
H	2.878984	-2.619238	1.679021
H	3.213076	-3.330546	0.090583
C	4.535866	-0.375032	1.390262
H	4.284233	-0.548058	2.445285
H	5.531763	0.089227	1.369206
C	3.494052	0.577422	0.740312
H	3.478542	1.528045	1.284479
C	2.123244	-0.114475	0.859341
H	1.976979	-0.416216	1.897482
C	3.910299	0.833186	-0.723026
H	3.216929	1.535867	-1.194943
H	4.901458	1.306644	-0.743472
C	-2.728199	-1.218261	-0.285661
C	-3.152422	-0.694363	-1.524176
C	-4.461804	-0.213708	-1.625452
H	-4.794233	0.193498	-2.578125
C	-5.354897	-0.252249	-0.549807
C	-4.914214	-0.813369	0.651333
H	-5.598515	-0.869940	1.495550
C	-3.614403	-1.307675	0.805643
C	-2.243908	-0.653133	-2.730244
H	-2.834650	-0.575853	-3.648474
H	-1.622641	-1.552485	-2.801084
H	-1.565605	0.206169	-2.697768
C	-6.752394	0.306433	-0.683845
H	-6.757951	1.395107	-0.541105
H	-7.430376	-0.124566	0.060093
H	-7.168608	0.109564	-1.677989
C	-3.213332	-1.943010	2.118640
H	-3.403979	-3.025068	2.112417
H	-3.793856	-1.521360	2.945147
H	-2.152702	-1.796567	2.341670
C	-1.231525	1.946327	0.676008
C	0.069960	0.953594	2.200299

H	0.182321	-0.021498	2.686922
C	-1.398013	1.385143	2.059662
H	-2.015964	0.485507	1.999248
H	-2.001829	1.735277	-0.074052
C	-2.004928	2.313678	3.122046
H	-3.048921	2.543076	2.874276
H	-1.992219	1.846111	4.115164
H	-1.464456	3.264140	3.190682
C	0.980338	1.987558	2.850147
H	0.654001	2.199602	3.879807
H	2.016096	1.642245	2.912672
H	0.982973	2.939865	2.306607
H	-0.915999	2.994266	0.646801
N	0.723268	2.764977	-1.812824
O	0.816296	3.620721	-2.668163

3.11

B3LYP SCF energy:	-1536.02641534 a.u.
B3LYP enthalpy:	-1535.364599 a.u.
B3LYP free energy:	-1535.470096 a.u.
M06 SCF energy in solution:	-1536.43822690 a.u.
M06 enthalpy in solution:	-1535.776411 a.u.
M06 free energy in solution:	-1535.881908 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.296125	0.866820	0.281549
O	1.071631	1.704964	-1.771191
O	1.194432	2.911060	0.033813
N	0.764258	-1.984588	0.226704
N	-1.412955	-1.792024	0.091567
C	-0.249087	-1.080477	0.177775
C	0.333194	-3.358999	-0.041014
H	0.797609	-4.067077	0.650753
H	0.594290	-3.660358	-1.065232
C	-1.185984	-3.250626	0.157079
H	-1.760343	-3.766766	-0.617806
H	-1.502801	-3.640761	1.133456
C	2.145258	-1.506249	0.080735
C	2.550286	-1.469847	-1.416003
H	1.836083	-0.850045	-1.970287
H	2.510678	-2.484617	-1.838907
C	3.972792	-0.895117	-1.565889
H	4.248522	-0.890333	-2.628671
C	4.968837	-1.764278	-0.774147
H	4.982441	-2.790579	-1.169329
H	5.986396	-1.365813	-0.885603
C	4.564994	-1.772972	0.714307
H	5.275767	-2.383292	1.287567
C	3.153770	-2.392819	0.846897
H	2.855234	-2.458148	1.901916
H	3.168457	-3.417665	0.445624
C	4.574511	-0.323092	1.251655
H	4.332204	-0.314668	2.323282
H	5.584891	0.098211	1.149620

C	3.550878	0.541315	0.463265
H	3.560532	1.565482	0.854306
C	2.162520	-0.093228	0.705260
H	2.092913	-0.246609	1.787816
C	3.982900	0.545769	-1.019607
H	3.323033	1.168933	-1.625518
H	4.994224	0.968256	-1.101753
C	-2.745061	-1.303838	-0.096965
C	-3.190766	-1.052820	-1.413022
C	-4.509903	-0.636377	-1.603498
H	-4.854557	-0.432592	-2.615193
C	-5.399099	-0.479400	-0.532657
C	-4.939387	-0.772352	0.752461
H	-5.620955	-0.677494	1.595700
C	-3.625202	-1.196431	0.994129
C	-2.272238	-1.247250	-2.598407
H	-2.774838	-0.961311	-3.527093
H	-1.962741	-2.295504	-2.698713
H	-1.355995	-0.653423	-2.510829
C	-6.810903	0.005518	-0.766406
H	-6.838809	1.096009	-0.891479
H	-7.465720	-0.245059	0.074379
H	-7.240238	-0.433419	-1.673961
C	-3.212595	-1.570110	2.399582
H	-2.131263	-1.508231	2.540765
H	-3.518463	-2.598266	2.636739
H	-3.692836	-0.917524	3.136477
C	-1.740369	2.115360	-0.911239
H	-2.067238	1.231601	-1.441388
C	-0.219031	0.969259	2.061333
H	-1.040248	0.388313	2.509993
C	-2.168448	2.381188	0.342340
H	-2.805167	1.651592	0.840063
C	-1.962271	3.694382	1.045050
H	-2.884856	4.289736	0.988961
H	-1.735587	3.561616	2.107886
H	-1.151160	4.267589	0.587943
H	-1.187608	2.853331	-1.483167
C	0.439803	1.876479	3.057687
H	-0.292604	2.419694	3.673567
H	1.019500	1.247608	3.756377
H	1.128404	2.590669	2.597644
O	1.984760	3.699584	-1.854870
N	1.440180	2.807761	-1.225456

3.12

B3LYP SCF energy:	-1418.12464492 a.u.
B3LYP enthalpy:	-1417.550645 a.u.
B3LYP free energy:	-1417.643262 a.u.
M06 SCF energy in solution:	-1418.58692432 a.u.
M06 enthalpy in solution:	-1418.012924 a.u.
M06 free energy in solution:	-1418.105541 a.u.

Cartesian coordinates

ATOM	X	Y	Z

Ru	-0.309338	0.900446	-0.522082
O	0.487957	2.429573	0.835372
O	-0.897750	3.130949	-0.687820
N	-0.784329	-1.741242	0.440211
N	1.396130	-1.486276	0.524969
C	0.235095	-0.888600	0.154146
C	-0.360481	-2.859461	1.285423
H	-0.823146	-3.800725	0.975854
H	-0.618155	-2.679042	2.339351
C	1.164874	-2.845468	1.059721
H	1.737358	-2.999635	1.978760
H	1.474503	-3.603926	0.329794
C	-2.145785	-1.211769	0.276675
C	-2.595958	-0.420799	1.533613
H	-1.845587	0.346550	1.778500
H	-2.653051	-1.093356	2.401866
C	-3.964845	0.240755	1.277177
H	-4.274893	0.791076	2.175025
C	-5.001608	-0.855573	0.954539
H	-5.112114	-1.537034	1.810039
H	-5.985901	-0.400969	0.779458
C	-4.553094	-1.637411	-0.297389
H	-5.291036	-2.416588	-0.529218
C	-3.186796	-2.310329	-0.018493
H	-2.862574	-2.899490	-0.886493
H	-3.284108	-3.002347	0.831963
C	-4.438527	-0.659303	-1.488801
H	-4.151355	-1.202984	-2.399074
H	-5.419293	-0.202742	-1.684205
C	-3.387739	0.436620	-1.170824
H	-3.308783	1.126892	-2.019871
C	-2.036361	-0.264432	-0.947590
H	-1.831778	-0.897963	-1.816691
C	-3.840194	1.211293	0.084361
H	-3.124752	2.011922	0.310616
H	-4.807985	1.696290	-0.103590
C	2.722844	-0.991486	0.292092
C	3.304048	-0.110938	1.224032
C	4.607184	0.339364	0.985540
H	5.060754	1.022505	1.700561
C	5.339204	-0.061003	-0.135469
C	4.741453	-0.956291	-1.027755
H	5.299005	-1.291692	-1.900218
C	3.443100	-1.437069	-0.834021
C	2.561629	0.358025	2.452812
H	3.266332	0.694956	3.219773
H	1.941843	-0.435261	2.883804
H	1.899569	1.197944	2.215203
C	6.730435	0.472382	-0.387360
H	6.699322	1.379472	-1.005492
H	7.351993	-0.259060	-0.915153
H	7.234620	0.735135	0.548591
C	2.863406	-2.431849	-1.815122
H	3.026728	-3.466015	-1.481812
H	3.342560	-2.333369	-2.794255
H	1.785691	-2.300509	-1.950344
C	0.502647	0.715441	-2.148157

H	1.185949	-0.114118	-2.369857
O	-0.032898	4.563348	0.733592
N	-0.151011	3.437116	0.301248
C	0.360019	1.702140	-3.271811
H	1.344308	2.100371	-3.562942
H	-0.045254	1.190314	-4.159748
H	-0.293869	2.541897	-3.022839

3.13

B3LYP SCF energy:	-1496.70937437 a.u.
B3LYP enthalpy:	-1496.077119 a.u.
B3LYP free energy:	-1496.177201 a.u.
M06 SCF energy in solution:	-1497.14232971 a.u.
M06 enthalpy in solution:	-1496.510074 a.u.
M06 free energy in solution:	-1496.610156 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.269356	0.967328	0.331471
O	1.211557	1.863815	-1.638205
O	1.268850	2.971326	0.231838
N	0.612882	-1.900801	0.135854
N	-1.552820	-1.602800	0.015801
C	-0.356078	-0.948303	0.134593
C	0.119115	-3.239650	-0.196314
H	0.549461	-4.000382	0.460736
H	0.369094	-3.503202	-1.233442
C	-1.393203	-3.071668	0.005377
H	-1.987927	-3.520871	-0.795481
H	-1.733266	-3.496324	0.959583
C	2.018613	-1.490648	0.021373
C	2.447379	-1.427207	-1.467397
H	1.776940	-0.749371	-2.008258
H	2.358330	-2.422955	-1.926599
C	3.902604	-0.928870	-1.577378
H	4.195011	-0.906047	-2.635552
C	4.836373	-1.877637	-0.801048
H	4.798356	-2.890492	-1.228261
H	5.876160	-1.533979	-0.886694
C	4.409727	-1.909528	0.680720
H	5.077212	-2.575389	1.244248
C	2.965626	-2.456419	0.771183
H	2.645986	-2.540403	1.818728
H	2.933315	-3.466970	0.335916
C	4.488802	-0.480039	1.265026
H	4.229462	-0.493127	2.332707
H	5.522521	-0.112586	1.192298
C	3.526799	0.463762	0.490451
H	3.586576	1.472827	0.915562
C	2.101111	-0.102181	0.689613
H	2.009407	-0.287167	1.766465
C	3.986461	0.490520	-0.984298
H	3.376736	1.172249	-1.578936
H	5.023021	0.852823	-1.034407
C	-2.868850	-1.054353	-0.115176

C	-3.349642	-0.763666	-1.411941
C	-4.652475	-0.282712	-1.550400
H	-5.022323	-0.048445	-2.546506
C	-5.495976	-0.099636	-0.446089
C	-5.007153	-0.436000	0.816359
H	-5.655088	-0.325692	1.684066
C	-3.706403	-0.925677	1.006130
C	-2.483944	-0.983811	-2.632091
H	-2.999139	-0.647680	-3.536775
H	-2.241278	-2.045778	-2.766163
H	-1.531160	-0.448079	-2.563694
C	-6.890545	0.453800	-0.624328
H	-6.868827	1.542678	-0.763255
H	-7.519060	0.246316	0.247581
H	-7.381113	0.026756	-1.506245
C	-3.272250	-1.336640	2.395199
H	-2.206072	-1.565639	2.441865
H	-3.822677	-2.227447	2.724849
H	-3.481892	-0.546357	3.125336
C	-1.591706	2.185331	-0.780161
H	-2.119695	1.432914	-1.349563
C	-0.290853	1.020341	2.111376
H	-1.051832	0.361131	2.553546
C	-1.881999	2.396858	0.533377
H	-2.635903	1.805351	1.042521
O	2.245823	3.797399	-1.551028
N	1.601883	2.913471	-1.011128
H	-0.993147	2.891625	-1.341945
C	0.257220	1.992757	3.113823
H	0.837864	1.420083	3.857046
H	0.917308	2.742730	2.670018
H	-0.544129	2.495747	3.676457
H	-1.495837	3.266955	1.055106

3.15

B3LYP SCF energy:	-1496.71777081 a.u.
B3LYP enthalpy:	-1496.083214 a.u.
B3LYP free energy:	-1496.178109 a.u.
M06 SCF energy in solution:	-1497.15197226 a.u.
M06 enthalpy in solution:	-1496.517415 a.u.
M06 free energy in solution:	-1496.612310 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.351748	0.906896	0.224345
O	-0.722724	2.104326	-1.391838
O	1.008873	2.951152	-0.389685
N	0.724081	-1.995267	0.297015
N	-1.444760	-1.682551	0.174337
C	-0.246879	-1.035116	0.273303
C	0.221854	-3.326549	-0.050126
H	0.668440	-4.101597	0.578851
H	0.437826	-3.568942	-1.100603
C	-1.282199	-3.153348	0.197751
H	-1.905872	-3.617220	-0.571139

H	-1.581199	-3.554504	1.173786
C	2.065186	-1.510433	-0.032260
C	2.215955	-1.350249	-1.570524
H	1.391412	-0.732979	-1.954802
H	2.137015	-2.331804	-2.059245
C	3.566303	-0.697856	-1.909732
H	3.660939	-0.597839	-2.998942
C	4.705826	-1.584563	-1.367310
H	4.682816	-2.569502	-1.855010
H	5.679475	-1.134541	-1.603712
C	4.555961	-1.740166	0.160493
H	5.368693	-2.367664	0.549021
C	3.201237	-2.419459	0.480476
H	3.090353	-2.573754	1.561651
H	3.163283	-3.409335	0.001027
C	4.625080	-0.340011	0.810169
H	4.567750	-0.422186	1.903803
H	5.591774	0.126971	0.573444
C	3.463506	0.546729	0.282455
H	3.525926	1.537688	0.738126
C	2.148929	-0.153928	0.696056
H	2.202665	-0.380187	1.764318
C	3.611308	0.691179	-1.247298
H	2.817930	1.334365	-1.649715
H	4.562593	1.190262	-1.477471
C	-2.754577	-1.138913	-0.049349
C	-3.092953	-0.659538	-1.330858
C	-4.389614	-0.177089	-1.536610
H	-4.653698	0.199794	-2.522436
C	-5.353548	-0.176213	-0.524393
C	-4.998588	-0.701693	0.720968
H	-5.738857	-0.729106	1.518143
C	-3.715541	-1.193648	0.979003
C	-2.113538	-0.674627	-2.480759
H	-2.648008	-0.622428	-3.434494
H	-1.502891	-1.584258	-2.484384
H	-1.433538	0.182467	-2.436969
C	-6.734469	0.386080	-0.768582
H	-6.752660	1.471908	-0.606315
H	-7.474058	-0.057341	-0.093581
H	-7.063499	0.208009	-1.798181
C	-3.404843	-1.778219	2.338631
H	-3.584658	-2.861869	2.359267
H	-4.045030	-1.332973	3.106643
H	-2.362709	-1.615165	2.629293
C	-1.361071	1.282435	1.403701
C	0.695076	1.429364	2.328036
C	-0.633384	2.165571	2.385642
H	-1.780611	0.398463	1.876009
H	-1.078827	2.222883	3.395127
H	0.648653	0.503532	2.910414
C	1.913224	2.258233	2.691535
H	2.832336	1.669577	2.761396
H	2.072815	3.077914	1.982047
H	1.747878	2.713188	3.681732
H	-2.071738	1.738172	0.709326
N	0.110024	3.088769	-1.304308

O	0.051450	4.061093	-2.025826
H	-0.525262	3.189506	2.009364

3.16

B3LYP SCF energy:	-1496.72453047 a.u.
B3LYP enthalpy:	-1496.090787 a.u.
B3LYP free energy:	-1496.186569 a.u.
M06 SCF energy in solution:	-1497.15895055 a.u.
M06 enthalpy in solution:	-1496.525207 a.u.
M06 free energy in solution:	-1496.620989 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.275328	0.985587	0.128628
O	1.037735	2.152996	-1.242456
O	-0.451372	3.235119	-0.083003
N	-1.023961	-1.757051	-0.426659
N	1.154841	-1.769600	-0.175745
C	0.049081	-0.968589	-0.134332
C	-0.699139	-3.181817	-0.511408
H	-1.177665	-3.658314	-1.372647
H	-1.022386	-3.710618	0.395601
C	0.830653	-3.138256	-0.631204
H	1.329794	-3.886710	-0.010073
H	1.168370	-3.274940	-1.667160
C	-2.369340	-1.213547	-0.300335
C	-3.105573	-1.793900	0.935517
H	-2.501458	-1.632042	1.834598
H	-3.221167	-2.879712	0.811778
C	-4.490830	-1.136569	1.090033
H	-4.994534	-1.564751	1.966400
C	-5.333842	-1.397740	-0.173322
H	-5.490452	-2.476796	-0.312147
H	-6.326740	-0.941669	-0.063556
C	-4.609787	-0.803057	-1.397879
H	-5.205043	-0.979717	-2.303088
C	-3.237969	-1.497658	-1.558323
H	-2.714785	-1.130862	-2.450581
H	-3.383608	-2.580277	-1.686621
C	-4.422731	0.717152	-1.192447
H	-3.949647	1.167703	-2.074883
H	-5.402330	1.200071	-1.073964
C	-3.554310	0.975514	0.073988
H	-3.412389	2.054544	0.205757
C	-2.199353	0.308540	-0.195273
H	-1.851643	0.685191	-1.204323
C	-4.303825	0.378967	1.287039
H	-3.765243	0.571168	2.218765
H	-5.283218	0.868239	1.378557
C	2.531615	-1.361495	-0.203312
C	3.350408	-1.674892	0.900847
C	4.699120	-1.314124	0.854703
H	5.332196	-1.541887	1.709894
C	5.255209	-0.672252	-0.257338
C	4.427441	-0.419908	-1.353374

H	4.847284	0.051278	-2.239723
C	3.068882	-0.760214	-1.357081
C	2.810349	-2.408808	2.107258
H	3.495849	-2.315713	2.955030
H	2.690262	-3.482369	1.905548
H	1.831812	-2.028723	2.415499
C	6.707212	-0.254570	-0.265808
H	6.833723	0.738341	0.185736
H	7.103134	-0.200304	-1.285340
H	7.329994	-0.952108	0.304928
C	2.240233	-0.478722	-2.589311
H	1.429504	-1.201855	-2.721196
H	2.869947	-0.511236	-3.484579
H	1.787531	0.516520	-2.535987
C	-1.069631	0.944487	2.138797
C	1.168078	1.112895	1.719556
C	0.161107	1.606259	2.736417
H	1.482308	0.094409	1.951529
H	0.376827	1.334741	3.784991
H	-1.241984	-0.061191	2.528332
H	-1.981869	1.538880	2.201318
C	2.370025	1.999719	1.438563
H	2.075586	3.033933	1.229391
H	3.007679	2.024672	2.338267
H	2.983944	1.639484	0.609303
N	0.472012	3.291574	-0.969884
O	0.805242	4.320610	-1.519245
H	0.073252	2.698041	2.686812

TS3.7-monodentateNO3

B3LYP SCF energy:	-1536.00941184 a.u.
B3LYP enthalpy:	-1535.348797 a.u.
B3LYP free energy:	-1535.450126 a.u.
M06 SCF energy in solution:	-1536.43168049 a.u.
M06 enthalpy in solution:	-1535.771066 a.u.
M06 free energy in solution:	-1535.872395 a.u.
Imaginary frequency:	-174.2899 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.334003	0.765807	-0.139498
O	-1.380717	2.663318	-0.515874
O	-2.130808	3.299327	1.455746
N	-0.559532	-2.121634	-0.120138
N	1.580222	-1.765486	0.184198
C	0.379240	-1.144566	-0.031938
C	-0.054902	-3.453478	0.224424
H	-0.413274	-4.214574	-0.474356
H	-0.375946	-3.739763	1.235236
C	1.462223	-3.240045	0.145983
H	2.006993	-3.692115	0.980100
H	1.885254	-3.630413	-0.788353
C	-1.978484	-1.747779	-0.091518
C	-2.520534	-1.785611	1.361312
H	-1.883200	-1.155282	1.992638

H	-2.472400	-2.811935	1.753306
C	-3.975935	-1.280112	1.393413
H	-4.345916	-1.317072	2.426652
C	-4.844516	-2.187995	0.498630
H	-4.836894	-3.219218	0.880942
H	-5.888580	-1.848252	0.517729
C	-4.307641	-2.151217	-0.947589
H	-4.924458	-2.796483	-1.587225
C	-2.851361	-2.674294	-0.969373
H	-2.459894	-2.683267	-1.995709
H	-2.825529	-3.710130	-0.598745
C	-4.356480	-0.698489	-1.466746
H	-4.007186	-0.654257	-2.507767
H	-5.395055	-0.339475	-1.464460
C	-3.477594	0.215635	-0.572439
H	-3.517611	1.240396	-0.950759
C	-2.035275	-0.311410	-0.635305
H	-1.728047	-0.345526	-1.708678
C	-4.017067	0.170432	0.872120
H	-3.422406	0.828785	1.515784
H	-5.048034	0.548107	0.894498
C	2.896593	-1.199238	0.116804
C	3.585437	-0.894816	1.304545
C	4.895804	-0.403522	1.211214
H	5.428859	-0.163335	2.129209
C	5.534802	-0.221451	-0.014979
C	4.834322	-0.563206	-1.179300
H	5.319476	-0.443970	-2.146027
C	3.530542	-1.059962	-1.139617
C	2.974979	-1.090753	2.674185
H	2.826164	-0.129662	3.182106
H	3.638417	-1.687046	3.311581
H	2.005531	-1.589767	2.623867
C	6.937268	0.334957	-0.093663
H	6.929570	1.380462	-0.428203
H	7.551566	-0.226461	-0.806824
H	7.435673	0.304574	0.880290
C	2.837665	-1.450547	-2.426780
H	1.789583	-1.136663	-2.444748
H	2.851802	-2.538333	-2.576398
H	3.342125	-1.001701	-3.287672
C	-0.000840	1.099669	1.652541
H	0.605949	0.490491	2.330220
C	1.492886	1.817007	-1.011851
H	2.102336	0.977384	-1.329072
C	1.674400	2.214270	0.322212
H	2.366944	1.614559	0.905854
C	1.416368	3.618405	0.814726
H	1.545216	3.692584	1.897878
H	2.131991	4.306860	0.341972
H	0.407441	3.952344	0.565734
C	1.098113	2.771314	-2.121162
H	1.979854	3.348318	-2.439389
H	0.737969	2.224068	-2.999420
H	0.315093	3.465323	-1.814982
H	-0.506905	1.971012	2.079229
O	-3.275214	3.721131	-0.353089

N	-2.298193	3.239197	0.222873

TS3.7

B3LYP SCF energy:	-1536.01999353 a.u.
B3LYP enthalpy:	-1535.358479 a.u.
B3LYP free energy:	-1535.456292 a.u.
M06 SCF energy in solution:	-1536.43716588 a.u.
M06 enthalpy in solution:	-1535.775651 a.u.
M06 free energy in solution:	-1535.873464 a.u.
Imaginary frequency:	-227.5934 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.372163	0.812326	0.282362
O	-1.323965	2.813707	0.395697
O	-0.800941	2.207690	-1.627150
N	-0.770994	-2.006466	-0.241107
N	1.397826	-1.822589	0.000776
C	0.225556	-1.110646	-0.033489
C	-0.337604	-3.402380	-0.163458
H	-0.778991	-4.007952	-0.960085
H	-0.623778	-3.845040	0.800808
C	1.182741	-3.257052	-0.299838
H	1.741150	-3.889176	0.396171
H	1.530074	-3.481854	-1.317096
C	-2.162763	-1.554770	-0.152171
C	-2.727031	-1.762372	1.275503
H	-2.057475	-1.289078	2.001699
H	-2.764560	-2.836516	1.509531
C	-4.139652	-1.154159	1.371575
H	-4.525280	-1.296132	2.390229
C	-5.063894	-1.866757	0.363586
H	-5.137082	-2.936506	0.607417
H	-6.080348	-1.454927	0.424467
C	-4.506289	-1.679070	-1.062652
H	-5.157619	-2.190442	-1.783935
C	-3.088782	-2.295092	-1.147626
H	-2.686559	-2.197042	-2.164602
H	-3.142178	-3.369811	-0.916216
C	-4.453907	-0.170099	-1.384808
H	-4.096839	-0.010128	-2.410874
H	-5.466620	0.254233	-1.329076
C	-3.513182	0.549892	-0.382189
H	-3.491731	1.618067	-0.619009
C	-2.111346	-0.064433	-0.542730
H	-1.845221	-0.023653	-1.608659
C	-4.062629	0.352264	1.044985
H	-3.418661	0.865607	1.769271
H	-5.061651	0.802604	1.126171
C	2.728136	-1.317993	-0.177569
C	3.645680	-1.421354	0.883864
C	4.962081	-0.992334	0.674345
H	5.672463	-1.062461	1.495552
C	5.387674	-0.485047	-0.555590
C	4.457316	-0.419075	-1.599571

H	4.772537	-0.039384	-2.569369
C	3.131054	-0.829920	-1.439632
C	3.246814	-2.003729	2.220587
H	3.951668	-1.702882	3.001884
H	3.243279	-3.102091	2.195162
H	2.242115	-1.689807	2.518715
C	6.806820	-0.005881	-0.754716
H	7.188049	-0.284118	-1.743574
H	7.481275	-0.424533	-0.000864
H	6.869774	1.087782	-0.680972
C	2.161154	-0.720137	-2.593942
H	1.423054	0.073214	-2.424125
H	1.596576	-1.646120	-2.750056
H	2.693136	-0.491381	-3.522084
C	-0.246954	0.568433	2.142707
H	0.208544	-0.250387	2.714120
C	1.647922	1.891745	0.207658
H	2.252012	1.172657	-0.332665
C	1.549258	1.670655	1.606762
H	2.116374	0.820636	1.977139
C	1.399151	2.831005	2.572676
H	1.267886	2.486138	3.602270
H	2.304067	3.454200	2.539944
H	0.548851	3.465614	2.309484
C	1.672191	3.282519	-0.384779
H	2.673488	3.717356	-0.240447
H	1.474108	3.253722	-1.458119
H	0.950771	3.958229	0.078796
H	-0.740729	1.306014	2.788194
O	-1.852301	4.104816	-1.296277
N	-1.344604	3.080121	-0.868878

TS3.8

B3LYP SCF energy:	-1536.02191790 a.u.
B3LYP enthalpy:	-1535.360412 a.u.
B3LYP free energy:	-1535.458405 a.u.
M06 SCF energy in solution:	-1536.43716343 a.u.
M06 enthalpy in solution:	-1535.775658 a.u.
M06 free energy in solution:	-1535.873651 a.u.
Imaginary frequency:	-218.1681 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.302514	0.893695	0.186298
O	1.498859	1.720932	-1.750936
O	1.310328	2.881479	0.078414
N	0.677042	-1.987571	0.158841
N	-1.488121	-1.737485	-0.011640
C	-0.304739	-1.052760	0.091253
C	0.212210	-3.354911	-0.088818
H	0.642375	-4.060078	0.627463
H	0.489277	-3.683386	-1.099888
C	-1.304762	-3.200929	0.071439
H	-1.875318	-3.707798	-0.712337
H	-1.657860	-3.572053	1.042935

C	2.084897	-1.581907	0.098869
C	2.623073	-1.669165	-1.352752
H	1.995747	-1.053646	-2.008198
H	2.565673	-2.707314	-1.711812
C	4.085366	-1.178617	-1.403498
H	4.455254	-1.262813	-2.433940
C	4.955761	-2.039528	-0.467217
H	4.947079	-3.090851	-0.790226
H	5.999770	-1.700948	-0.509867
C	4.420361	-1.923481	0.974392
H	5.041605	-2.526605	1.650204
C	2.971979	-2.462770	1.012042
H	2.574258	-2.439955	2.035782
H	2.966911	-3.512515	0.681085
C	4.455788	-0.443223	1.418445
H	4.112286	-0.351993	2.458319
H	5.491990	-0.076832	1.391241
C	3.561031	0.412955	0.478829
H	3.591675	1.459141	0.804761
C	2.123368	-0.133223	0.612485
H	1.914954	-0.182502	1.694240
C	4.132453	0.293211	-0.951235
H	3.569755	0.914240	-1.649992
H	5.172019	0.650235	-0.957959
C	-2.823218	-1.230025	-0.120034
C	-3.362753	-1.016433	-1.407814
C	-4.677129	-0.557852	-1.514747
H	-5.090653	-0.378118	-2.504963
C	-5.478321	-0.334772	-0.387585
C	-4.937188	-0.614014	0.868354
H	-5.554144	-0.479731	1.754936
C	-3.623063	-1.075992	1.027285
C	-2.562522	-1.320780	-2.654963
H	-3.060418	-0.918474	-3.542181
H	-2.460014	-2.404576	-2.801460
H	-1.549981	-0.909174	-2.614611
C	-6.885784	0.195226	-0.532603
H	-6.885401	1.283230	-0.680149
H	-7.487207	-0.014453	0.357798
H	-7.392988	-0.246752	-1.397397
C	-3.138646	-1.450286	2.410777
H	-2.051067	-1.529287	2.463360
H	-3.558519	-2.418302	2.715834
H	-3.463843	-0.715346	3.155310
C	-1.286237	1.763876	-1.027170
H	-1.792114	0.984177	-1.580647
C	-0.616343	1.199989	1.816581
H	-1.422055	0.570210	2.204277
C	-1.808521	2.155054	0.237128
H	-2.652199	1.571403	0.597449
C	-1.800245	3.617602	0.628995
H	-2.575596	4.139529	0.051413
H	-2.023666	3.775297	1.687600
H	-0.836940	4.080097	0.398998
H	-0.822159	2.530361	-1.643093
C	-0.125722	2.201105	2.827322
H	-0.942088	2.737694	3.331217

H	0.405210	1.635751	3.610281
H	0.576369	2.923845	2.404068
O	2.470334	3.681416	-1.603316
N	1.786986	2.791744	-1.121004

TS3.10'

B3LYP SCF energy:	-1535.99618155 a.u.
B3LYP enthalpy:	-1535.335006 a.u.
B3LYP free energy:	-1535.433988 a.u.
M06 SCF energy in solution:	-1536.41625131 a.u.
M06 enthalpy in solution:	-1535.755076 a.u.
M06 free energy in solution:	-1535.854058 a.u.
Imaginary frequency:	-109.1007 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.240243	0.943001	0.275833
O	-1.223888	2.936997	0.194898
O	-0.561975	2.059316	-1.672216
N	-0.753217	-1.922879	-0.168064
N	1.420095	-1.750965	0.041572
C	0.249150	-1.035661	0.017060
C	-0.322161	-3.322546	-0.118696
H	-0.763877	-3.905312	-0.931514
H	-0.621464	-3.783216	0.832303
C	1.199301	-3.187053	-0.242006
H	1.747158	-3.812500	0.468379
H	1.558039	-3.427434	-1.251318
C	-2.157802	-1.491295	-0.160637
C	-2.820841	-1.774301	1.210100
H	-2.223040	-1.340198	2.013118
H	-2.866643	-2.859554	1.386872
C	-4.244107	-1.183824	1.229361
H	-4.700285	-1.371302	2.211049
C	-5.083817	-1.863523	0.129408
H	-5.159816	-2.942932	0.325347
H	-6.107454	-1.464987	0.132393
C	-4.426736	-1.611562	-1.243114
H	-5.016510	-2.101397	-2.029558
C	-2.997949	-2.213629	-1.245358
H	-2.524664	-2.076120	-2.226565
H	-3.063186	-3.297166	-1.058532
C	-4.380573	-0.088131	-1.496965
H	-3.961102	0.122546	-2.489478
H	-5.404965	0.313132	-1.490545
C	-3.514805	0.597686	-0.406120
H	-3.491940	1.677500	-0.592662
C	-2.094018	0.003566	-0.498218
H	-1.816613	0.047893	-1.561346
C	-4.163460	0.335428	0.968698
H	-3.585556	0.826104	1.762020
H	-5.172792	0.769822	0.995924
C	2.753882	-1.259445	-0.143200
C	3.660123	-1.337399	0.930358
C	4.976387	-0.908641	0.725408

H	5.679426	-0.959489	1.554264
C	5.411238	-0.422312	-0.511063
C	4.491459	-0.382723	-1.565065
H	4.816183	-0.025243	-2.540249
C	3.164731	-0.797528	-1.410841
C	3.236464	-1.867302	2.280951
H	4.002298	-1.662095	3.034996
H	3.082189	-2.954253	2.261217
H	2.295038	-1.420250	2.615934
C	6.830176	0.060545	-0.703567
H	7.505878	-0.373062	0.040771
H	6.894208	1.152509	-0.607163
H	7.209651	-0.197805	-1.698272
C	2.210124	-0.727676	-2.581151
H	1.667894	-1.668553	-2.728380
H	2.752705	-0.508494	-3.505587
H	1.454377	0.053500	-2.440240
C	-0.493538	0.456318	2.364226
H	-0.314776	-0.585316	2.617561
H	-1.473523	0.833962	2.655075
C	1.591015	1.619419	0.178898
H	2.443047	1.067157	0.584751
C	0.593525	1.368517	2.371924
H	1.581007	0.941332	2.530146
C	2.101940	2.813341	-0.563171
H	2.720450	3.412773	0.124874
H	2.789218	2.483520	-1.358580
H	1.338256	3.453092	-1.004964
C	0.433292	2.794575	2.846612
H	0.488454	2.814173	3.945296
H	1.219476	3.452708	2.462677
H	-0.531525	3.211794	2.548032
N	-1.172480	3.029347	-1.087709
O	-1.658299	3.962876	-1.698715

TS3.9

B3LYP SCF energy:	-1496.70896418 a.u.
B3LYP enthalpy:	-1496.077210 a.u.
B3LYP free energy:	-1496.172693 a.u.
M06 SCF energy in solution:	-1497.14366531 a.u.
M06 enthalpy in solution:	-1496.511911 a.u.
M06 free energy in solution:	-1496.607394 a.u.
Imaginary frequency:	-123.8859 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.265473	0.987159	0.291664
O	1.345493	1.833163	-1.648188
O	1.280941	2.974636	0.201298
N	0.604989	-1.888786	0.128945
N	-1.559135	-1.593949	-0.004757
C	-0.362867	-0.936813	0.115982
C	0.112929	-3.233224	-0.183639
H	0.539630	-3.982469	0.488664
H	0.370449	-3.513129	-1.214414

C	-1.399900	-3.062656	0.005393
H	-1.989212	-3.521926	-0.793713
H	-1.746325	-3.474776	0.962737
C	2.016264	-1.493428	0.044266
C	2.498742	-1.494116	-1.429647
H	1.855092	-0.832675	-2.021003
H	2.417085	-2.506772	-1.851523
C	3.963068	-1.013836	-1.505492
H	4.293317	-1.036417	-2.552487
C	4.858217	-1.939434	-0.658670
H	4.825660	-2.968214	-1.046394
H	5.903664	-1.608103	-0.719814
C	4.378224	-1.909399	0.806747
H	5.017691	-2.559059	1.419539
C	2.926164	-2.438013	0.865515
H	2.567747	-2.476766	1.903192
H	2.897865	-3.464707	0.469534
C	4.448606	-0.459633	1.339367
H	4.146233	-0.429886	2.395409
H	5.487805	-0.103396	1.294690
C	3.528026	0.461697	0.490715
H	3.583033	1.485772	0.878702
C	2.089521	-0.079851	0.650167
H	1.939155	-0.207580	1.731841
C	4.043938	0.426388	-0.965005
H	3.465200	1.093829	-1.605061
H	5.086817	0.773061	-0.989038
C	-2.878218	-1.050393	-0.127568
C	-3.370550	-0.760163	-1.419670
C	-4.672370	-0.272061	-1.545229
H	-5.050570	-0.035952	-2.537711
C	-5.504575	-0.085983	-0.433392
C	-5.007642	-0.431161	0.824047
H	-5.648450	-0.322514	1.697162
C	-3.708048	-0.927465	1.000944
C	-2.525578	-1.000791	-2.650727
H	-3.037766	-0.639088	-3.547185
H	-2.326879	-2.070835	-2.794503
H	-1.551926	-0.504045	-2.590989
C	-6.896887	0.477475	-0.597168
H	-6.870038	1.568520	-0.716908
H	-7.523570	0.258081	0.273180
H	-7.392459	0.068443	-1.484710
C	-3.267754	-1.359969	2.381755
H	-2.187208	-1.502576	2.445171
H	-3.746436	-2.308336	2.660017
H	-3.560325	-0.623678	3.138725
C	-1.410184	2.051275	-0.801655
H	-1.945810	1.337775	-1.412313
C	-0.488215	1.172272	2.013769
H	-1.268721	0.524822	2.430707
C	-1.806182	2.264869	0.520289
H	-2.643132	1.707765	0.927988
O	2.373367	3.767496	-1.529498
N	1.693807	2.892174	-1.019018
H	-0.892398	2.839758	-1.335713
C	-0.009535	2.196598	3.004914

H	0.527248	1.659018	3.803390
H	0.677698	2.924046	2.565068
H	-0.840945	2.726705	3.493085
H	-1.567208	3.208772	1.000321

TS3.11

B3LYP SCF energy:	-1496.70717925 a.u.
B3LYP enthalpy:	-1496.075711 a.u.
B3LYP free energy:	-1496.170197 a.u.
M06 SCF energy in solution:	-1497.14310145 a.u.
M06 enthalpy in solution:	-1496.511633 a.u.
M06 free energy in solution:	-1496.606119 a.u.
Imaginary frequency:	-200.2683 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.338312	0.861051	0.440990
O	-1.310578	2.849098	0.633724
O	-0.630007	2.369175	-1.376799
N	-0.725128	-1.896099	-0.341229
N	1.443886	-1.722097	-0.084730
C	0.265291	-1.021495	-0.039148
C	-0.279251	-3.287636	-0.417396
H	-0.724187	-3.810529	-1.268615
H	-0.548313	-3.832516	0.498458
C	1.238035	-3.111663	-0.555188
H	1.810821	-3.819284	0.050099
H	1.571080	-3.206176	-1.597571
C	-2.120584	-1.458139	-0.235609
C	-2.717150	-1.806430	1.150772
H	-2.068133	-1.405253	1.936292
H	-2.753998	-2.898626	1.276986
C	-4.133784	-1.212240	1.271827
H	-4.543216	-1.454167	2.261910
C	-5.032279	-1.822031	0.176649
H	-5.109150	-2.910525	0.312451
H	-6.050821	-1.417938	0.253975
C	-4.441837	-1.494759	-1.210585
H	-5.073887	-1.934115	-1.993823
C	-3.021080	-2.099276	-1.320120
H	-2.594255	-1.903861	-2.312563
H	-3.078479	-3.191218	-1.194438
C	-4.389102	0.038781	-1.381226
H	-4.009593	0.300066	-2.377913
H	-5.405031	0.452127	-1.306620
C	-3.473938	0.657486	-0.291469
H	-3.450078	1.744247	-0.418051
C	-2.067305	0.063550	-0.482350
H	-1.785550	0.202659	-1.536131
C	-4.052074	0.318703	1.097335
H	-3.422858	0.756715	1.881827
H	-5.052742	0.760089	1.203816
C	2.766456	-1.180159	-0.201098
C	3.691174	-1.418002	0.834077
C	4.998317	-0.942559	0.686425

H	5.712921	-1.117503	1.488192
C	5.410174	-0.255793	-0.459691
C	4.476097	-0.060469	-1.482038
H	4.781752	0.456974	-2.388982
C	3.156187	-0.514519	-1.382027
C	3.303228	-2.185706	2.077329
H	4.035235	-2.028111	2.875266
H	3.260416	-3.266435	1.886163
H	2.316528	-1.891209	2.448613
C	6.819396	0.275420	-0.582687
H	6.904667	1.276502	-0.139456
H	7.126610	0.357003	-1.630513
H	7.538356	-0.369793	-0.066458
C	2.187341	-0.271304	-2.516994
H	1.443506	0.491505	-2.257609
H	1.630056	-1.175730	-2.785187
H	2.720482	0.070504	-3.409114
C	-0.330051	0.453074	2.276323
H	0.077562	-0.416346	2.807700
C	1.682580	2.010326	0.578884
H	2.276428	1.456226	-0.140395
C	1.566593	1.444149	1.858848
H	2.113525	0.537046	2.084794
O	-1.730366	4.233409	-1.014254
N	-1.242476	3.191594	-0.608080
H	-0.816916	1.165519	2.957071
C	1.631022	3.503077	0.362305
H	2.638567	3.920424	0.504614
H	1.318296	3.748701	-0.655481
H	0.956181	3.997094	1.066257
H	1.372878	2.108144	2.698871

TS3.18

B3LYP SCF energy:	-1536.01451892 a.u.
B3LYP enthalpy:	-1535.353048 a.u.
B3LYP free energy:	-1535.449742 a.u.
M06 SCF energy in solution:	-1536.43121933 a.u.
M06 enthalpy in solution:	-1535.769748 a.u.
M06 free energy in solution:	-1535.866442 a.u.
Imaginary frequency:	-214.5273 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.410854	0.833347	0.420212
O	-1.383470	2.822801	0.575248
O	-0.726288	2.304254	-1.433152
N	-0.779884	-1.942129	-0.312518
N	1.394887	-1.759827	-0.144588
C	0.214997	-1.060104	-0.045166
C	-0.334018	-3.330904	-0.412187
H	-0.817001	-3.854401	-1.241676
H	-0.555937	-3.878642	0.514937
C	1.170847	-3.144623	-0.623362
H	1.777048	-3.857641	-0.059196
H	1.451440	-3.219295	-1.682964

C	-2.175580	-1.505440	-0.227022
C	-2.783138	-1.816170	1.162613
H	-2.138960	-1.396717	1.942493
H	-2.821935	-2.904782	1.316274
C	-4.199894	-1.216788	1.256163
H	-4.617787	-1.429583	2.249384
C	-5.090530	-1.856042	0.171436
H	-5.169411	-2.940296	0.336480
H	-6.109241	-1.449220	0.229476
C	-4.489220	-1.568123	-1.219797
H	-5.115327	-2.029359	-1.995196
C	-3.068381	-2.176898	-1.300560
H	-2.633468	-2.010266	-2.294927
H	-3.129308	-3.264627	-1.144710
C	-4.433200	-0.040412	-1.434211
H	-4.045601	0.191950	-2.434989
H	-5.448959	0.376541	-1.379541
C	-3.525685	0.608153	-0.355371
H	-3.501414	1.690702	-0.513036
C	-2.118342	0.006830	-0.518965
H	-1.827632	0.113546	-1.573504
C	-4.116290	0.308743	1.037772
H	-3.495930	0.769916	1.815858
H	-5.118192	0.752273	1.121161
C	2.713310	-1.229612	-0.332323
C	3.718386	-1.570425	0.593401
C	5.018117	-1.097511	0.377371
H	5.792931	-1.350346	1.098490
C	5.346370	-0.319055	-0.734758
C	4.334929	-0.033357	-1.658852
H	4.575660	0.548647	-2.546187
C	3.021262	-0.481237	-1.489829
C	3.435167	-2.454445	1.787253
H	4.125732	-2.235424	2.607923
H	3.565842	-3.515939	1.534979
H	2.411673	-2.331485	2.152321
C	6.748428	0.208412	-0.932641
H	7.018584	0.239113	-1.993807
H	7.487120	-0.409458	-0.411557
H	6.845622	1.231214	-0.544842
C	1.979155	-0.152615	-2.533511
H	1.299703	0.638675	-2.196481
H	1.354499	-1.018681	-2.778572
H	2.458250	0.187837	-3.456493
C	-0.448551	0.459291	2.256704
H	0.004915	-0.376558	2.801947
C	1.627579	1.940443	0.613112
H	2.377586	1.255990	0.227173
C	1.299916	1.779694	1.977846
C	1.650335	3.313838	-0.022641
H	2.636996	3.767114	0.157127
H	1.497067	3.272624	-1.102880
H	0.898661	3.978025	0.412158
H	-1.025530	1.126000	2.913753
H	0.797697	2.631762	2.435893
C	2.200165	0.984744	2.905355
H	1.727212	0.748729	3.862907

H	2.534266	0.058228	2.434602
H	3.094137	1.587368	3.119096
O	-1.824042	4.173746	-1.094916
N	-1.329749	3.139964	-0.675756

TS3.21

B3LYP SCF energy:	-1536.01855539 a.u.
B3LYP enthalpy:	-1535.356806 a.u.
B3LYP free energy:	-1535.454163 a.u.
M06 SCF energy in solution:	-1536.43422044 a.u.
M06 enthalpy in solution:	-1535.772471 a.u.
M06 free energy in solution:	-1535.869828 a.u.
Imaginary frequency:	-241.2579 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.352682	0.940273	0.246824
O	1.539691	1.810687	-1.694387
O	1.436404	2.887791	0.192597
N	0.657408	-1.950992	0.146528
N	-1.502787	-1.660435	0.008443
C	-0.308058	-0.995417	0.105248
C	0.168229	-3.307476	-0.109364
H	0.592552	-4.025250	0.597811
H	0.432708	-3.631964	-1.125123
C	-1.342770	-3.129165	0.065426
H	-1.928946	-3.609825	-0.723286
H	-1.694631	-3.511797	1.032245
C	2.072226	-1.578734	0.076749
C	2.591377	-1.652430	-1.383263
H	1.969046	-1.012865	-2.020265
H	2.507469	-2.682747	-1.758946
C	4.062647	-1.190954	-1.444027
H	4.418197	-1.265437	-2.480244
C	4.926648	-2.084677	-0.532960
H	4.893509	-3.129866	-0.873735
H	5.976567	-1.765911	-0.582416
C	4.410555	-1.983143	0.916842
H	5.027487	-2.610070	1.574674
C	2.952107	-2.494331	0.962987
H	2.567315	-2.482491	1.991833
H	2.921889	-3.537317	0.612905
C	4.480965	-0.511874	1.385382
H	4.150686	-0.431341	2.430385
H	5.523835	-0.165608	1.352430
C	3.593311	0.378209	0.470641
H	3.648749	1.417465	0.814115
C	2.148007	-0.143817	0.614000
H	1.950287	-0.206063	1.696817
C	4.144085	0.271702	-0.968427
H	3.584429	0.914886	-1.649510
H	5.189903	0.609603	-0.983294
C	-2.829384	-1.155101	-0.172136
C	-3.270078	-0.860746	-1.481143
C	-4.592541	-0.450787	-1.663554

H	-4.932859	-0.210941	-2.668803
C	-5.494213	-0.358065	-0.595042
C	-5.040976	-0.702491	0.679465
H	-5.730299	-0.654422	1.520240
C	-3.720037	-1.109630	0.914816
C	-2.349271	-1.023892	-2.669164
H	-2.839088	-0.685710	-3.587109
H	-2.070103	-2.076045	-2.812094
H	-1.417737	-0.461723	-2.550880
C	-6.912896	0.110546	-0.820473
H	-7.559873	-0.149638	0.023328
H	-7.342018	-0.332308	-1.726389
H	-6.955064	1.200664	-0.944015
C	-3.304759	-1.515811	2.310575
H	-2.231716	-1.387464	2.472461
H	-3.542892	-2.571133	2.501666
H	-3.838841	-0.927336	3.063854
C	-1.268686	1.968191	-0.864406
H	-2.029560	1.323384	-1.289663
C	-0.532575	1.263019	1.886083
H	-1.403996	0.694274	2.228954
C	-1.517482	2.526820	0.417290
H	-0.684159	2.532772	-1.582680
C	-0.000912	2.210068	2.929835
H	-0.788038	2.856562	3.347121
H	0.388110	1.609948	3.767099
H	0.812764	2.836487	2.554614
H	-0.942033	3.417625	0.660094
C	-2.895874	2.475120	1.045451
H	-2.873651	2.661537	2.124356
H	-3.507669	3.267731	0.592599
H	-3.397836	1.523701	0.861065
O	2.612342	3.709833	-1.465985
N	1.890725	2.833415	-1.017463

3.26

B3LYP SCF energy:	-2018.36200465 a.u.
B3LYP enthalpy:	-2017.847508 a.u.
B3LYP free energy:	-2017.950265 a.u.
M06 SCF energy in solution:	-2018.88886134 a.u.
M06 enthalpy in solution:	-2018.374365 a.u.
M06 free energy in solution:	-2018.477122 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.156203	1.362190	-0.037302
Cl	0.763925	1.596019	-2.333214
C	-0.010011	-0.602653	0.070587
N	-1.103664	-1.403088	0.161847
N	1.092312	-1.401064	0.136759
C	-0.758503	-2.837952	0.223207
H	-1.283379	-3.319199	1.053567
H	-1.060431	-3.337404	-0.705417
C	0.763138	-2.810504	0.410096
H	1.291650	-3.469877	-0.284467

H	1.064597	-3.075275	1.430746
C	-1.554229	1.962070	-0.159869
H	-2.453252	1.346725	-0.201058
Cl	0.487714	1.732272	2.296982
C	-2.488372	-1.045149	0.059492
C	-5.221551	-0.456632	-0.122162
C	-3.092222	-0.977771	-1.210375
C	-3.222690	-0.827793	1.239485
C	-4.584976	-0.531140	1.121309
C	-4.457186	-0.678157	-1.273340
H	-5.161372	-0.351212	2.026236
H	-4.933130	-0.612475	-2.249452
C	2.471994	-0.990516	0.072708
C	5.170717	-0.240031	-0.086964
C	3.181312	-0.713193	1.257725
C	3.121358	-1.003482	-1.181507
C	4.460687	-0.613149	-1.233945
C	4.520684	-0.319590	1.145590
H	4.964020	-0.605350	-2.198170
H	5.069214	-0.080695	2.054250
C	2.421810	-1.469104	-2.435869
H	1.611062	-0.791319	-2.715968
H	1.996603	-2.473304	-2.311538
H	3.128575	-1.511557	-3.270022
C	2.587103	-0.916157	2.631645
H	3.020499	-0.212948	3.348299
H	2.809902	-1.930901	2.992458
H	1.507637	-0.767382	2.649835
C	6.602513	0.231303	-0.184165
H	6.646632	1.300803	-0.428604
H	7.148811	-0.302505	-0.969691
H	7.137722	0.089787	0.760585
C	-2.292065	-1.172184	-2.477311
H	-2.937153	-1.080648	-3.356149
H	-1.820035	-2.161743	-2.518207
H	-1.491237	-0.428613	-2.565165
C	-2.559953	-0.872234	2.596132
H	-2.097535	-1.847760	2.793053
H	-3.292529	-0.689125	3.387857
H	-1.768231	-0.118492	2.680515
C	-6.701859	-0.168888	-0.219561
H	-7.285369	-1.099330	-0.222594
H	-6.946279	0.369770	-1.141227
H	-7.050516	0.430565	0.627835
C	-1.757208	3.444616	-0.212871
H	-2.285214	3.714470	-1.139678
H	-2.383942	3.761521	0.634218
H	-0.821626	4.014974	-0.175277

TS3.27

B3LYP SCF energy:	-2175.58915930 a.u.
B3LYP enthalpy:	-2174.956822 a.u.
B3LYP free energy:	-2175.065025 a.u.
M06 SCF energy in solution:	-2176.03783512 a.u.
M06 enthalpy in solution:	-2175.405498 a.u.

M06 free energy in solution: -2175.513701 a.u.
Imaginary frequency: -206.5483 cm-1

Cartesian coordinates

ATOM	X	Y	Z
N	1.024691	-1.853182	0.194846
C	0.646978	-3.273066	0.357891
H	0.961890	-3.849836	-0.518647
C	-0.880738	-3.198775	0.501440
N	-1.166219	-1.769505	0.244692
H	-1.224749	-3.474425	1.504468
C	2.413245	-1.479036	0.087511
C	-2.536689	-1.330466	0.199118
C	-5.247927	-0.611309	0.122149
C	-3.179813	-0.942188	1.390712
C	-3.235046	-1.406306	-1.021874
C	-4.584082	-1.033972	-1.033717
C	-4.528635	-0.574756	1.320666
C	-2.460048	-0.922167	2.717385
C	-2.569243	-1.868166	-2.295585
H	-5.128976	-1.080669	-1.974248
H	-5.030932	-0.262957	2.234027
C	-6.714653	-0.248009	0.085852
C	5.132691	-0.807905	-0.106405
C	3.033817	-1.470527	-1.179243
C	3.154946	-1.251012	1.266494
C	4.503324	-0.902205	1.139046
C	4.386622	-1.116631	-1.246649
C	2.302920	-1.865960	-2.439665
C	2.550297	-1.419620	2.639268
H	5.078598	-0.712307	2.042576
H	4.870054	-1.097751	-2.220909
C	6.581477	-0.392407	-0.213278
H	-2.047556	-1.907529	2.969620
H	-1.625429	-0.212408	2.718029
H	-2.109918	-2.858069	-2.181843
H	-1.779824	-1.174667	-2.605768
H	-7.002425	0.162584	-0.887814
H	-6.963885	0.491464	0.854221
H	-7.345268	-1.129101	0.265989
H	2.245613	-2.459926	2.816625
H	1.674541	-0.779652	2.775864
H	3.001378	-1.915607	-3.280597
H	1.514705	-1.150244	-2.694194
H	7.046828	-0.789195	-1.121665
H	7.163121	-0.739241	0.647773
H	6.676703	0.701000	-0.249081
C	-0.044890	-1.031440	0.110677
Ru	0.105312	1.027202	-0.151280
Cl	0.370952	1.326914	2.288807
Cl	-0.052989	0.772379	-2.608980
C	-1.445872	2.077700	-0.032046
H	3.281973	-1.160512	3.410441
H	1.835062	-2.853631	-2.343175
H	-3.302322	-1.937992	-3.105053
H	-3.149287	-0.641902	3.519925
H	-1.407893	-3.826670	-0.222894

H	1.136424	-3.697842	1.238991
C	0.167989	3.386912	-0.497466
C	1.422465	2.696628	-0.599023
H	-0.298047	3.580862	-1.461340
H	1.711770	2.444258	-1.618132
C	-0.064551	4.433504	0.576522
H	0.619078	5.277153	0.411692
H	-1.086454	4.823569	0.541336
H	0.121823	4.031893	1.575522
H	-1.673308	2.424641	0.982067
C	2.582275	2.922075	0.341947
H	2.268487	3.118329	1.366714
H	3.246735	2.051501	0.352504
H	3.172593	3.777762	-0.022322
C	-2.544907	2.323497	-1.019785
H	-3.389655	1.679216	-0.738591
H	-2.901171	3.362260	-0.945320
H	-2.260394	2.093228	-2.045934

TS3.29

B3LYP SCF energy:	-2175.58716842 a.u.
B3LYP enthalpy:	-2174.954893 a.u.
B3LYP free energy:	-2175.063588 a.u.
M06 SCF energy in solution:	-2176.03520093 a.u.
M06 enthalpy in solution:	-2175.402926 a.u.
M06 free energy in solution:	-2175.511621 a.u.
Imaginary frequency:	-184.9525 cm-1

Cartesian coordinates

ATOM	X	Y	Z
N	1.040645	-1.822024	0.242175
C	0.673664	-3.233897	0.482048
H	1.194083	-3.888023	-0.223228
C	-0.847370	-3.222038	0.277355
N	-1.149339	-1.777771	0.157497
H	-1.394097	-3.655202	1.119445
C	2.429510	-1.436591	0.197254
C	-2.522970	-1.364109	0.040972
C	-5.242086	-0.703262	-0.166640
C	-3.273698	-1.160277	1.215285
C	-3.118124	-1.291872	-1.233739
C	-4.472924	-0.948120	-1.308390
C	-4.626239	-0.825837	1.083128
C	-2.658391	-1.299768	2.586617
C	-2.344076	-1.589561	-2.495206
H	-4.939802	-0.884730	-2.288977
H	-5.212602	-0.662122	1.984775
C	-6.696878	-0.309561	-0.279854
C	5.154574	-0.769187	0.097220
C	3.119458	-1.527562	-1.030554
C	3.102596	-1.104953	1.391254
C	4.456940	-0.759203	1.307751
C	4.472648	-1.176574	-1.054017
C	2.448017	-2.017529	-2.290081
C	2.426622	-1.157283	2.740083

H	4.981405	-0.491009	2.222241
H	5.008548	-1.233610	-1.998972
C	6.607545	-0.359795	0.032207
H	-2.284818	-2.316934	2.763664
H	-1.817079	-0.610943	2.717562
H	-1.917979	-2.601024	-2.479671
H	-1.514338	-0.888961	-2.639441
H	-7.154800	-0.722821	-1.184795
H	-6.809884	0.781777	-0.327968
H	-7.274599	-0.656915	0.583390
H	2.045598	-2.163367	2.958716
H	1.583705	-0.462381	2.804387
H	3.170218	-2.067547	-3.110518
H	1.635746	-1.349668	-2.591930
H	7.156559	-0.946144	-0.712752
H	7.104339	-0.486908	0.999751
H	6.707765	0.696671	-0.250098
C	-0.036461	-1.017025	0.102716
Ru	0.099514	1.054829	-0.108809
Cl	-0.107633	1.305938	2.346345
Cl	0.380057	0.837617	-2.559420
C	-1.446746	2.043103	-0.505811
H	3.139122	-0.901038	3.530100
H	2.028667	-3.023587	-2.160424
H	-3.000385	-1.525543	-3.368504
H	-3.401032	-1.086516	3.361490
H	-1.155984	-3.744572	-0.635173
H	0.959992	-3.529358	1.497573
C	0.233522	3.417654	-0.404620
C	1.440413	2.740811	-0.026738
H	-1.647257	2.164269	-1.576097
H	0.147335	3.635011	-1.468646
C	-2.591348	2.426542	0.378544
H	-3.063642	3.356609	0.032875
H	-3.345520	1.633225	0.273129
H	-2.326521	2.499779	1.432922
C	-0.336430	4.455664	0.543833
H	-1.324022	4.812183	0.240910
H	-0.392067	4.066883	1.564021
H	0.338482	5.322099	0.547402
C	2.640573	2.626763	-0.940657
H	3.279005	3.510870	-0.786642
H	3.246014	1.746623	-0.697904
H	2.356212	2.568690	-1.991742
H	1.690605	2.830699	1.031549

3.30

B3LYP SCF energy:	-1325.79426306 a.u.
B3LYP enthalpy:	-1325.241358 a.u.
B3LYP free energy:	-1325.341001 a.u.
M06 SCF energy in solution:	-1326.24801714 a.u.
M06 enthalpy in solution:	-1325.695112 a.u.
M06 free energy in solution:	-1325.794755 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.404764	0.988373	-0.416466
O	0.575464	1.975046	1.529907
O	1.273405	3.151255	-0.208654
N	0.868443	-1.799082	0.085292
N	-1.316559	-1.565928	-0.056917
C	-0.139819	-0.877414	-0.084954
C	0.379041	-3.179444	-0.054929
C	-1.112214	-2.998415	0.238986
C	2.245232	-1.423991	-0.042969
C	3.202233	-1.918117	0.862066
C	4.529516	-1.494601	0.721714
C	4.920406	-0.572152	-0.253366
C	3.940414	-0.067130	-1.111481
C	2.604304	-0.488835	-1.048744
C	2.836993	-2.835906	2.006141
C	6.362511	-0.138486	-0.381078
C	1.555265	0.089822	-1.938924
C	-2.627417	-1.007810	0.118868
C	-3.575489	-1.180015	-0.909613
C	-4.863437	-0.671820	-0.721981
C	-5.231741	-0.010127	0.454301
C	-4.269931	0.134272	1.457327
C	-2.966515	-0.359073	1.321490
C	-3.217983	-1.874972	-2.203330
C	-6.639190	0.507007	0.643382
C	-1.974028	-0.176896	2.445924
C	-1.038638	1.440844	-1.448345
C	1.088541	3.046927	1.033132
C	1.468946	4.163160	1.981008
H	0.862783	-3.865761	0.641376
H	0.556649	-3.540501	-1.078009
H	-1.750754	-3.627499	-0.386096
H	-1.353733	-3.200967	1.291969
H	5.271513	-1.873085	1.422083
H	4.213215	0.665311	-1.868093
H	1.869261	-2.564189	2.441804
H	3.590949	-2.776088	2.796958
H	2.779316	-3.889537	1.699318
H	6.884267	-0.712648	-1.158736
H	6.910005	-0.286470	0.555845
H	6.438995	0.919511	-0.654639
H	1.013761	-0.679252	-2.499453
H	1.966660	0.826161	-2.635784
H	-5.594491	-0.789518	-1.519490
H	-4.538664	0.642328	2.381215
H	-2.242406	-1.549154	-2.578876
H	-3.968700	-1.668406	-2.972211
H	-3.170629	-2.966039	-2.084413
H	-7.311545	-0.287988	0.993312
H	-7.054505	0.890863	-0.295018
H	-6.673688	1.312823	1.383732
H	-1.269470	0.637288	2.239563
H	-1.374970	-1.079257	2.612748
H	-2.496884	0.054627	3.379491
H	-1.906236	0.782652	-1.575082
H	0.600598	4.448373	2.584360

H	2.241978	3.809089	2.672135
H	1.839620	5.028816	1.428777
C	-1.165893	2.750526	-2.175001
H	-2.079268	3.276662	-1.855586
H	-0.309064	3.407558	-2.008924
H	-1.274959	2.566420	-3.256194

3.35

B3LYP SCF energy:	-1325.78815128 a.u.
B3LYP enthalpy:	-1325.235781 a.u.
B3LYP free energy:	-1325.337660 a.u.
M06 SCF energy in solution:	-1326.24510729 a.u.
M06 enthalpy in solution:	-1325.692737 a.u.
M06 free energy in solution:	-1325.794616 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.062284	1.160862	-0.063066
O	-2.062711	1.752807	0.070926
O	-0.589998	3.354944	-0.330253
N	1.370486	-1.550426	-0.078380
N	-0.821168	-1.687783	-0.242492
C	0.208177	-0.816528	-0.051334
C	1.120775	-2.916872	-0.588281
C	-0.375571	-3.086875	-0.330727
C	2.685863	-0.986409	-0.160022
C	3.764886	-1.626146	0.477078
C	5.045057	-1.068389	0.346987
C	5.271457	0.112309	-0.359810
C	4.167029	0.757165	-0.927906
C	2.870553	0.239630	-0.841959
C	3.596878	-2.846553	1.356091
C	6.662790	0.683900	-0.505730
C	1.705255	1.014752	-1.365348
C	-2.221144	-1.397388	-0.100044
C	-3.006267	-1.274891	-1.258605
C	-4.380582	-1.066535	-1.111738
C	-4.982469	-0.979133	0.146567
C	-4.169422	-1.096124	1.277865
C	-2.791139	-1.304729	1.181488
C	-2.387903	-1.340005	-2.635699
C	-6.475095	-0.784828	0.282780
C	-1.945680	-1.389262	2.429976
C	1.045520	1.364964	1.463910
C	-1.786546	2.986235	-0.151962
C	-2.921421	3.986334	-0.186884
H	1.721335	-3.668199	-0.077868
H	1.361471	-2.952007	-1.660049
H	-0.893889	-3.617774	-1.134000
H	-0.578272	-3.612294	0.613249
H	5.879420	-1.564134	0.839453
H	4.309747	1.699745	-1.452822
H	2.638533	-2.832789	1.886501
H	4.393213	-2.880073	2.106371
H	3.653874	-3.788929	0.793777

H	7.075087	0.480110	-1.503206
H	7.352406	0.252673	0.227657
H	6.665779	1.772059	-0.374067
H	1.248797	0.515713	-2.241400
H	2.019975	2.017122	-1.676909
H	-4.993925	-0.963117	-2.004506
H	-4.617939	-1.016531	2.266128
H	-1.608441	-0.579371	-2.761269
H	-3.145700	-1.174761	-3.407423
H	-1.919439	-2.311972	-2.836844
H	-6.993769	-1.745958	0.401433
H	-6.897232	-0.294283	-0.600589
H	-6.720607	-0.174365	1.158548
H	-1.299225	-0.508533	2.521300
H	-1.292311	-2.269826	2.432645
H	-2.577649	-1.439875	3.321901
H	-2.561839	4.969382	-0.497002
H	-3.371511	4.060014	0.809729
H	-3.702617	3.637511	-0.869949
H	1.341594	0.504254	2.081756
C	1.504385	2.692067	1.995057
H	1.158472	2.836849	3.030358
H	2.605597	2.709127	2.027001
H	1.152681	3.527623	1.385237

TS3.31

B3LYP SCF energy:	-1482.99299768 a.u.
B3LYP enthalpy:	-1482.323242 a.u.
B3LYP free energy:	-1482.433442 a.u.
M06 SCF energy in solution:	-1483.38650292 a.u.
M06 enthalpy in solution:	-1482.716747 a.u.
M06 free energy in solution:	-1482.826947 a.u.
Imaginary frequency:	-178.5623 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.412671	-0.691257	0.051125
O	-1.378423	-3.333067	-1.937669
O	-1.740740	-2.418872	0.098002
N	-0.495372	2.183417	-0.232089
N	1.636445	1.694651	-0.361662
C	0.411984	1.153566	-0.126217
C	0.095290	3.393918	-0.831009
C	1.589332	3.152614	-0.597566
C	-1.897935	1.904053	-0.328629
C	-2.830693	2.691965	0.366684
C	-4.185378	2.352208	0.267969
C	-4.624760	1.246697	-0.470547
C	-3.671670	0.469659	-1.132007
C	-2.303686	0.787624	-1.106399
C	-2.410107	3.853213	1.237789
C	-6.095714	0.911100	-0.561926
C	-1.280234	-0.062627	-1.771829
C	2.915063	1.048831	-0.286618
C	3.447722	0.454388	-1.446836

C	4.714261	-0.131550	-1.369085
C	5.458722	-0.135770	-0.183998
C	4.901777	0.467300	0.947222
C	3.638634	1.070125	0.919389
C	2.664132	0.413434	-2.736885
C	6.835555	-0.756913	-0.138687
C	3.078042	1.708564	2.169808
C	1.193951	-1.676146	0.204510
C	-2.005433	-3.234310	-0.876624
H	-0.264103	4.305722	-0.349566
H	-0.155242	3.443902	-1.899623
H	2.210609	3.424902	-1.455581
H	1.962944	3.693843	0.281312
H	-4.913978	2.954340	0.807356
H	-3.985842	-0.401278	-1.701775
H	-1.471775	3.640886	1.761784
H	-3.177102	4.068834	1.988132
H	-2.261750	4.774930	0.658248
H	-6.543720	1.330648	-1.472815
H	-6.652977	1.313555	0.290744
H	-6.256264	-0.171892	-0.592079
H	-0.601375	0.508658	-2.414008
H	-1.692935	-0.918135	-2.304528
H	5.128051	-0.601308	-2.259015
H	5.462063	0.469087	1.879879
H	1.767843	-0.208472	-2.633081
H	3.273172	0.000777	-3.546564
H	2.327979	1.410994	-3.044140
H	7.588244	-0.084364	-0.571194
H	6.872211	-1.691219	-0.709707
H	7.143276	-0.975426	0.888901
H	2.038664	1.413460	2.346895
H	3.095951	2.804874	2.111621
H	3.666862	1.422686	3.046546
H	2.131191	-1.180004	0.466920
C	-0.707432	-0.428885	2.191805
C	0.298849	-1.447558	2.243015
H	-0.364336	0.574642	2.445671
H	1.290529	-1.097667	2.523427
C	-3.214510	-4.138005	-0.606102
H	-4.109625	-3.527931	-0.436308
H	-3.386001	-4.812063	-1.448384
H	-3.051280	-4.725502	0.305149
C	-0.030382	-2.860975	2.665264
H	-0.822773	-3.278038	2.039691
H	0.845705	-3.513101	2.608702
H	-0.374921	-2.862487	3.709602
C	-2.145596	-0.697781	2.596104
H	-2.787268	0.141721	2.308882
H	-2.533306	-1.600744	2.122899
H	-2.214387	-0.808388	3.689746
C	1.401554	-3.104421	-0.208771
H	0.505023	-3.577727	-0.606961
H	2.163443	-3.099210	-1.003554
H	1.822458	-3.705089	0.611912

TS3.34

B3LYP SCF energy:	-1482.99960790 a.u.
B3LYP enthalpy:	-1482.329438 a.u.
B3LYP free energy:	-1482.437286 a.u.
M06 SCF energy in solution:	-1483.38857176 a.u.
M06 enthalpy in solution:	-1482.718402 a.u.
M06 free energy in solution:	-1482.826250 a.u.
Imaginary frequency:	-240.8078 cm-1

Cartesian coordinates

ATOM	X	Y	Z
O	-0.749536	2.163225	-1.611841
O	0.647076	3.093254	-0.168459
C	1.312564	0.685576	1.753213
C	-0.094326	3.164542	-1.205126
H	1.337679	-0.241951	2.340476
C	-1.540528	1.313101	1.294544
C	-0.565804	1.398294	2.354956
H	-2.105701	0.389109	1.274608
H	-0.585438	0.550442	3.038426
C	-0.157425	4.473510	-1.971213
H	-1.123157	4.578544	-2.472432
H	0.625288	4.479410	-2.739874
H	0.019554	5.321094	-1.303725
Ru	0.302214	0.895986	0.153362
C	0.043803	-1.104010	-0.041831
C	1.531192	0.498165	-1.545720
N	1.130630	-1.944317	-0.166569
N	-1.058494	-1.864891	-0.303138
C	2.693543	-0.272385	-1.020730
H	0.945200	-0.070472	-2.277738
H	1.846094	1.438935	-2.004650
C	0.768696	-3.228694	-0.798998
C	2.477344	-1.471681	-0.300769
C	-0.739701	-3.279897	-0.572137
C	-2.443153	-1.485711	-0.285974
C	4.007828	0.192231	-1.139207
H	1.292142	-4.070384	-0.343276
H	1.028639	-3.198590	-1.866217
C	3.536653	-2.166541	0.298759
H	-1.297107	-3.640149	-1.441542
H	-1.007591	-3.904316	0.290135
C	-3.019396	-0.918361	-1.439073
C	-3.226451	-1.786988	0.845885
C	5.095020	-0.498589	-0.585822
H	4.181616	1.118681	-1.682813
C	4.839175	-1.668270	0.129990
C	3.322335	-3.395585	1.153315
C	-4.388542	-0.629047	-1.417099
C	-2.206974	-0.615307	-2.674747
C	-4.590008	-1.477917	0.816672
C	-2.625973	-2.417086	2.082625
C	6.505676	0.013362	-0.767308
H	5.666111	-2.203700	0.592424
H	2.379952	-3.338690	1.708939
H	4.136063	-3.503169	1.877735

H	3.301278	-4.320647	0.560284
C	-5.189683	-0.892660	-0.302318
H	-4.840199	-0.188814	-2.303789
H	-1.657951	0.325992	-2.559176
H	-2.861876	-0.521943	-3.547175
H	-1.473517	-1.401685	-2.883758
H	-5.196250	-1.697696	1.693275
H	-1.620180	-2.035304	2.284624
H	-2.546272	-3.508460	1.987002
H	-3.249685	-2.217314	2.959436
H	6.863462	-0.158478	-1.791346
H	7.204027	-0.485747	-0.087306
H	6.567855	1.092454	-0.583811
C	-6.658196	-0.536031	-0.301619
H	-6.809736	0.515560	-0.023965
H	-7.219710	-1.146516	0.413388
H	-7.104935	-0.675463	-1.292144
C	-2.374926	2.508998	0.891537
H	-2.836476	2.342706	-0.084205
H	-3.180911	2.656278	1.627923
H	-1.795414	3.432472	0.843076
C	-0.285141	2.738590	3.007806
H	0.469852	2.659815	3.794556
H	0.053558	3.472733	2.272539
H	-1.206079	3.120529	3.469653
C	2.412817	1.636030	2.137287
H	2.508524	1.771942	3.223799
H	3.351131	1.177695	1.788489
H	2.314923	2.608513	1.649171

3.36

B3LYP SCF energy:	-1418.13051205 a.u.
B3LYP enthalpy:	-1417.556611 a.u.
B3LYP free energy:	-1417.648604 a.u.
M06 SCF energy in solution:	-1418.59410000 a.u.
M06 enthalpy in solution:	-1418.020199 a.u.
M06 free energy in solution:	-1418.112192 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.231927	1.041275	0.260103
O	1.396355	2.326795	-0.471499
O	-0.317540	3.329972	0.420464
N	-0.975475	-1.593198	-0.661092
N	1.196050	-1.637910	-0.308484
C	0.090133	-0.854024	-0.251443
C	-0.640014	-3.009845	-0.839176
H	-1.088123	-3.422339	-1.747790
H	-0.989027	-3.603982	0.016739
C	0.897295	-2.956827	-0.906173
H	1.380941	-3.762106	-0.346686
H	1.265226	-2.990515	-1.940316
C	-2.313032	-1.057517	-0.379728
C	-2.827487	-1.569396	0.989158
H	-2.081053	-1.340865	1.757526

H	-2.950630	-2.661367	0.957648
C	-4.170308	-0.897543	1.334925
H	-4.523406	-1.273750	2.304382
C	-5.203290	-1.232932	0.240593
H	-5.373038	-2.318293	0.199030
H	-6.169645	-0.767398	0.477066
C	-4.692800	-0.718561	-1.121305
H	-5.425668	-0.955393	-1.903717
C	-3.352318	-1.415141	-1.466196
H	-2.985903	-1.085028	-2.447308
H	-3.506025	-2.503244	-1.523464
C	-4.499830	0.812020	-1.037312
H	-4.175416	1.210144	-2.008192
H	-5.460268	1.291477	-0.800946
C	-3.448343	1.149890	0.054025
H	-3.304920	2.236332	0.101754
C	-2.129627	0.474307	-0.349190
H	-1.903362	0.790823	-1.395321
C	-3.957631	0.627811	1.412119
H	-3.236813	0.868455	2.202208
H	-4.901841	1.126112	1.671751
C	2.556854	-1.199672	-0.160694
C	3.252701	-1.549323	1.012512
C	4.589205	-1.161151	1.135102
H	5.131077	-1.425830	2.040713
C	5.245101	-0.443101	0.129719
C	4.530650	-0.128114	-1.028408
H	5.025841	0.421301	-1.826355
C	3.190626	-0.492877	-1.199167
C	2.584059	-2.318892	2.127666
H	3.284747	-2.491758	2.950011
H	2.217246	-3.298032	1.795275
H	1.721700	-1.774597	2.527969
C	6.680088	-0.001640	0.300025
H	6.732288	1.017920	0.704205
H	7.215065	0.001709	-0.655849
H	7.222428	-0.655269	0.991447
C	2.468855	-0.098158	-2.466361
H	1.714286	-0.831607	-2.766997
H	3.178100	0.015253	-3.292571
H	1.961408	0.863841	-2.330020
C	-0.246522	0.638564	2.048045
H	0.020467	-0.355705	2.433201
O	1.349556	4.522392	-0.366078
N	0.824119	3.453280	-0.141964
C	-0.520952	1.646367	3.130997
H	-1.326302	1.288653	3.791720
H	0.370895	1.768873	3.765202
H	-0.796917	2.627706	2.736772

TS3.37

B3LYP SCF energy:	-1575.33621703 a.u.
B3LYP enthalpy:	-1574.644401 a.u.
B3LYP free energy:	-1574.744989 a.u.
M06 SCF energy in solution:	-1575.73592476 a.u.

M06 enthalpy in solution: -1575.044109 a.u.
M06 free energy in solution: -1575.144697 a.u.
Imaginary frequency: -230.6816 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.370126	0.817258	0.126153
O	-1.385690	2.790533	0.129317
O	-0.968640	2.096414	-1.888411
N	-0.689752	-2.051467	-0.186845
N	1.469255	-1.805858	0.072307
C	0.284819	-1.119917	-0.039799
C	-0.232750	-3.427913	0.011639
H	-0.646793	-4.103479	-0.742086
H	-0.531762	-3.796838	1.002533
C	1.285916	-3.265055	-0.104826
H	1.839720	-3.821828	0.656197
H	1.660837	-3.572049	-1.090011
C	-2.093885	-1.634255	-0.144454
C	-2.664173	-1.749137	1.290991
H	-2.016874	-1.195681	1.979751
H	-2.666056	-2.801025	1.612680
C	-4.098692	-1.187090	1.328576
H	-4.491572	-1.265336	2.351449
C	-4.986111	-2.005831	0.369024
H	-5.024010	-3.056509	0.691396
H	-6.016888	-1.627245	0.391702
C	-4.420955	-1.905714	-1.062934
H	-5.047987	-2.490993	-1.748664
C	-2.983861	-2.478542	-1.088504
H	-2.573222	-2.443641	-2.106263
H	-3.004746	-3.534041	-0.777001
C	-4.412295	-0.424483	-1.498324
H	-4.048489	-0.330832	-2.530041
H	-5.438837	-0.030822	-1.484054
C	-3.508647	0.400077	-0.543720
H	-3.521022	1.446717	-0.861662
C	-2.083191	-0.176049	-0.638396
H	-1.803309	-0.203179	-1.701575
C	-4.073379	0.291398	0.887146
H	-3.464629	0.886506	1.577428
H	-5.090685	0.705877	0.919095
C	2.803038	-1.309173	-0.110792
C	3.686156	-1.299163	0.984378
C	5.008091	-0.888286	0.773421
H	5.691744	-0.870903	1.619768
C	5.473670	-0.510962	-0.488294
C	4.578549	-0.560503	-1.563354
H	4.925191	-0.284516	-2.557088
C	3.248215	-0.958082	-1.403788
C	3.250485	-1.749918	2.359910
H	3.935144	-1.374819	3.126874
H	3.245784	-2.845703	2.439627
H	2.239616	-1.409416	2.600782
C	6.898067	-0.048241	-0.688346
H	7.296965	-0.385121	-1.651469
H	7.556492	-0.423288	0.101925

H	6.963832	1.047738	-0.676975
C	2.318113	-0.982737	-2.595390
H	1.542792	-0.211252	-2.517685
H	1.798354	-1.942470	-2.694797
H	2.875103	-0.807863	-3.520519
C	-0.126621	0.739911	2.013749
H	0.440536	-0.052095	2.519732
C	1.569268	1.832640	-0.166131
H	2.216268	1.069477	-0.580882
C	1.509359	1.844849	1.274052
H	2.163652	1.113939	1.744287
C	1.416187	3.173895	2.000193
H	1.393747	3.046294	3.085300
H	2.299979	3.779946	1.758220
H	0.531631	3.740584	1.698240
C	1.606658	3.122412	-0.957996
H	2.613120	3.562653	-0.875053
H	1.409397	2.938617	-2.016140
H	0.894345	3.869778	-0.603915
O	-2.058744	3.975447	-1.587492
N	-1.490410	2.986837	-1.146940
C	-0.935183	1.557492	2.991038
H	-1.703638	0.895856	3.417178
H	-0.335942	1.918560	3.838211
H	-1.442398	2.403583	2.521392

TS3.40

B3LYP SCF energy:	-1575.32385084 a.u.
B3LYP enthalpy:	-1574.632942 a.u.
B3LYP free energy:	-1574.736596 a.u.
M06 SCF energy in solution:	-1575.72500829 a.u.
M06 enthalpy in solution:	-1575.034099 a.u.
M06 free energy in solution:	-1575.137753 a.u.
Imaginary frequency:	-132.0763 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.356557	0.712167	-0.006794
O	-2.436106	2.971752	-1.656452
O	-1.538149	2.529159	0.308493
N	-0.463746	-2.170188	0.056308
N	1.674336	-1.749368	0.280005
C	0.444989	-1.168147	0.083309
C	0.081217	-3.472377	0.444971
H	-0.288707	-4.274472	-0.199055
H	-0.189852	-3.713515	1.482495
C	1.587499	-3.227857	0.287764
H	2.181928	-3.645441	1.105560
H	1.972750	-3.634508	-0.656103
C	-1.888641	-1.826636	-0.001877
C	-2.475762	-1.655692	1.424455
H	-1.878778	-0.916746	1.978183
H	-2.405145	-2.604752	1.976561
C	-3.944396	-1.194770	1.338937
H	-4.346546	-1.082128	2.354634

C	-4.760404	-2.255180	0.571788
H	-4.739608	-3.214975	1.108369
H	-5.812215	-1.945749	0.509975
C	-4.178816	-2.424333	-0.847254
H	-4.758758	-3.178524	-1.395888
C	-2.711626	-2.901630	-0.745576
H	-2.287979	-3.060136	-1.746438
H	-2.675856	-3.865857	-0.215310
C	-4.241036	-1.072059	-1.587565
H	-3.857110	-1.182304	-2.611117
H	-5.287082	-0.745158	-1.673257
C	-3.412155	-0.007562	-0.822239
H	-3.464566	0.940863	-1.361060
C	-1.948358	-0.484945	-0.770195
H	-1.614641	-0.684892	-1.799803
C	-4.004610	0.154323	0.593906
H	-3.455354	0.924001	1.148462
H	-5.046466	0.495883	0.527163
C	2.963377	-1.165328	0.032460
C	3.806376	-0.851194	1.113992
C	5.073158	-0.314054	0.843449
H	5.721412	-0.061908	1.680601
C	5.527532	-0.103692	-0.458365
C	4.687266	-0.476376	-1.515419
H	5.033802	-0.349744	-2.539161
C	3.419001	-1.019395	-1.299322
C	3.416347	-1.100790	2.553971
H	3.391729	-0.165993	3.126451
H	4.150153	-1.754191	3.041574
H	2.434236	-1.570086	2.637341
C	6.881523	0.510563	-0.726401
H	7.373495	0.038096	-1.583808
H	7.543571	0.415513	0.140184
H	6.791761	1.580686	-0.955207
C	2.593301	-1.473611	-2.483831
H	1.534317	-1.223905	-2.378427
H	2.661409	-2.561457	-2.618735
H	2.959902	-1.013362	-3.406381
C	0.731475	1.314574	1.850967
H	1.224432	0.399773	2.166432
C	0.879253	1.373480	-1.248289
H	1.843519	0.882863	-1.403797
C	1.466692	2.111496	0.946693
H	2.429241	1.708968	0.642095
C	-0.221581	1.885936	2.885138
H	0.355333	2.298986	3.726652
H	-0.861708	2.668311	2.477401
H	-0.866850	1.100198	3.295482
C	1.320834	3.609441	0.858590
H	1.787351	4.069733	1.742292
H	1.826323	4.014974	-0.022503
H	0.272128	3.910836	0.831138
O	-3.218758	3.894426	0.160466
N	-2.432618	3.148807	-0.424635
C	0.633048	2.499951	-2.203431
H	1.438773	3.247537	-2.137542
H	0.683501	2.088516	-3.224525

H	-0.340030	2.976460	-2.077566

TS3.40'

B3LYP SCF energy:	-1575.33106604 a.u.
B3LYP enthalpy:	-1574.639452 a.u.
B3LYP free energy:	-1574.739869 a.u.
M06 SCF energy in solution:	-1575.72768388 a.u.
M06 enthalpy in solution:	-1575.036070 a.u.
M06 free energy in solution:	-1575.136487 a.u.
Imaginary frequency:	-222.8024 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.302175	0.838066	0.240600
O	1.682970	1.779911	-1.460712
O	1.324859	2.812916	0.415815
N	0.741569	-1.982720	-0.280391
N	-1.420373	-1.738717	-0.526054
C	-0.261742	-1.075249	-0.190977
C	0.336519	-3.255700	-0.881743
H	0.759227	-4.108510	-0.343832
H	0.668912	-3.311599	-1.927162
C	-1.189507	-3.178532	-0.769399
H	-1.706197	-3.505915	-1.676568
H	-1.571431	-3.770638	0.072932
C	2.137775	-1.575457	-0.087754
C	2.859792	-1.379763	-1.445159
H	2.315447	-0.640620	-2.042779
H	2.866952	-2.327181	-2.004328
C	4.309452	-0.904665	-1.205636
H	4.811173	-0.787145	-2.175226
C	5.065878	-1.940352	-0.351494
H	5.116580	-2.908418	-0.871011
H	6.100713	-1.608528	-0.191724
C	4.346539	-2.103123	1.002787
H	4.884847	-2.832238	1.623420
C	2.916400	-2.627260	0.741989
H	2.387614	-2.805936	1.688180
H	2.974995	-3.590402	0.212272
C	4.295567	-0.739690	1.730030
H	3.816256	-0.854351	2.712267
H	5.319202	-0.383149	1.913663
C	3.515809	0.292189	0.866674
H	3.486143	1.254830	1.390623
C	2.080503	-0.258415	0.705682
H	1.745332	-0.523964	1.721169
C	4.280318	0.447156	-0.467491
H	3.826845	1.205563	-1.105239
H	5.308591	0.773856	-0.256651
C	-2.772246	-1.323644	-0.287254
C	-3.568151	-0.904835	-1.371604
C	-4.891489	-0.521386	-1.123512
H	-5.501291	-0.180412	-1.957916
C	-5.450155	-0.568712	0.155727
C	-4.655998	-1.051861	1.201746

H	-5.083549	-1.134377	2.199340
C	-3.330735	-1.451661	1.004186
C	-3.054204	-0.903442	-2.794404
H	-3.405959	-0.021260	-3.339858
H	-3.424702	-1.783696	-3.337249
H	-1.963236	-0.922962	-2.838567
C	-6.867735	-0.109790	0.406681
H	-6.890505	0.929063	0.761649
H	-7.358551	-0.722746	1.170591
H	-7.471180	-0.156050	-0.505613
C	-2.571647	-2.079199	2.154383
H	-1.491139	-1.945482	2.071672
H	-2.768921	-3.159156	2.199544
H	-2.894831	-1.658064	3.111977
C	-1.284116	1.775468	-1.010057
H	-1.711524	0.932112	-1.540501
C	-0.743433	0.978412	1.820862
H	-1.558169	0.307264	2.103264
C	-1.840179	2.016761	0.288665
H	-2.665018	1.360928	0.554511
C	-0.910384	2.918860	-1.929521
H	-1.829770	3.354237	-2.352208
H	-0.375050	3.724135	-1.422151
H	-0.292063	2.571010	-2.759259
C	-1.945974	3.433104	0.818361
H	-2.612445	4.016490	0.167620
H	-2.367630	3.459974	1.826643
H	-0.975135	3.934884	0.835000
O	2.670924	3.698809	-1.073679
N	1.923521	2.796702	-0.727922
C	-0.343550	1.890263	2.952223
H	-1.204246	2.362078	3.446778
H	0.147074	1.261707	3.712628
H	0.368043	2.662959	2.650907

3.41

B3LYP SCF energy:	-1979.03579316 a.u.
B3LYP enthalpy:	-1978.551488 a.u.
B3LYP free energy:	-1978.649665 a.u.
M06 SCF energy in solution:	-1979.58117039 a.u.
M06 enthalpy in solution:	-1979.096865 a.u.
M06 free energy in solution:	-1979.195042 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	3.163661	1.021805	0.969125
C	2.396457	-0.159366	0.921406
C	2.994960	-1.409336	0.657211
C	4.351840	-1.435114	0.327762
C	5.124464	-0.270579	0.276253
C	4.517098	0.939149	0.620941
N	1.003054	-0.134422	1.291474
C	0.631194	-0.228385	2.715813
C	-0.881452	-0.462876	2.649051
N	-1.194131	-0.160668	1.237663

C	-0.079608	-0.023478	0.473505
C	-2.568769	-0.220780	0.829150
C	-3.357536	0.941938	0.916546
C	-4.707935	0.847519	0.568170
C	-5.284377	-0.358222	0.151148
C	-4.470693	-1.493180	0.084632
C	-3.112381	-1.452686	0.422120
Ru	0.107756	0.426227	-1.444476
Cl	1.083706	-1.555657	-2.303637
C	-2.765520	2.261897	1.349543
C	-6.751169	-0.427011	-0.205915
C	-2.259726	-2.694457	0.299942
C	2.220700	-2.701619	0.762915
C	6.576413	-0.321234	-0.136860
C	2.601995	2.335648	1.458379
Cl	0.207425	2.776786	-1.100361
C	-1.566559	0.251972	-2.101779
H	1.172192	-1.047188	3.197991
H	0.887038	0.704226	3.231927
H	-1.446825	0.197984	3.311954
H	-1.159214	-1.498258	2.881736
H	-2.478035	-0.080486	-1.608494
H	-1.658939	0.513966	-3.169843
H	-5.324713	1.742153	0.622422
H	-4.900238	-2.437965	-0.240898
H	4.816975	-2.393296	0.107809
H	5.112877	1.849120	0.636462
H	3.280874	3.156712	1.209631
H	1.630401	2.565719	1.018108
H	2.491952	2.327859	2.552122
H	2.889371	-3.556804	0.627413
H	1.741887	-2.809219	1.744737
H	1.441925	-2.761377	-0.001905
H	7.157534	0.477801	0.335897
H	7.035570	-1.279975	0.126809
H	6.678097	-0.199545	-1.223317
H	-2.867253	-3.547016	-0.017304
H	-1.456538	-2.560243	-0.433996
H	-1.784821	-2.965062	1.250905
H	-3.528946	3.045471	1.343903
H	-2.354130	2.209571	2.365901
H	-1.950074	2.571899	0.686780
H	-7.014950	-1.400654	-0.630191
H	-7.382586	-0.266623	0.677336
H	-7.020729	0.344044	-0.937288

TS3.42

B3LYP SCF energy:	-2136.26989020 a.u.
B3LYP enthalpy:	-2135.667767 a.u.
B3LYP free energy:	-2135.774037 a.u.
M06 SCF energy in solution:	-2136.73685495 a.u.
M06 enthalpy in solution:	-2136.134732 a.u.
M06 free energy in solution:	-2136.241002 a.u.
Imaginary frequency:	-207.2349 cm-1

Cartesian coordinates

ATOM	X	Y	Z
N	0.922005	-1.810967	0.303030
C	0.509894	-3.187878	0.645999
H	0.956748	-3.904591	-0.049333
C	-1.021316	-3.116264	0.530718
N	-1.268610	-1.676166	0.293126
H	-1.531582	-3.442960	1.441374
C	2.316964	-1.459682	0.209008
C	-2.624808	-1.204980	0.178569
C	-5.302273	-0.392433	-0.020376
C	-3.323841	-0.844806	1.347424
C	-3.255776	-1.217451	-1.080452
C	-4.589226	-0.798013	-1.151919
C	-4.655500	-0.436385	1.218487
C	-2.678045	-0.895664	2.710746
C	-2.542541	-1.674603	-2.330126
H	-5.083621	-0.799332	-2.121039
H	-5.201573	-0.151103	2.115231
C	-6.731420	0.085976	-0.132066
C	5.047036	-0.835063	0.020916
C	2.982829	-1.633413	-1.023388
C	3.015101	-1.063097	1.368729
C	4.372156	-0.742358	1.241338
C	4.339519	-1.301926	-1.091237
C	2.282914	-2.190955	-2.238775
C	2.358448	-1.013783	2.727280
H	4.916781	-0.427737	2.128877
H	4.857622	-1.423264	-2.039998
C	6.503146	-0.448920	-0.094200
H	-2.295298	-1.897341	2.945055
H	-1.836695	-0.197644	2.777933
H	-2.128149	-2.684340	-2.217357
H	-1.711449	-1.009340	-2.589406
H	-7.229743	-0.339811	-1.009354
H	-6.776436	1.178930	-0.230155
H	-7.315231	-0.182667	0.755105
H	1.934467	-1.987096	3.005264
H	1.549667	-0.277049	2.762741
H	2.993360	-2.315192	-3.061583
H	1.482851	-1.526097	-2.578349
H	7.030197	-1.082051	-0.816286
H	7.017494	-0.529246	0.869173
H	6.609871	0.589212	-0.435918
C	-0.126819	-0.975116	0.141501
Ru	0.093226	1.044919	-0.242199
Cl	-0.049573	1.551650	2.167294
Cl	0.228979	0.674448	-2.677464
C	-1.481483	1.972292	-0.506050
H	3.093419	-0.748162	3.493252
H	1.840652	-3.174577	-2.035088
H	-3.236355	-1.698775	-3.176083
H	-3.404301	-0.633568	3.486230
H	-1.409877	-3.705526	-0.307117
H	0.844781	-3.440673	1.657985
C	0.169774	3.414985	-0.776080
C	1.426979	2.762710	-0.633067

H	-1.960171	2.019933	-1.487948
H	-0.174192	3.494868	-1.804901
H	1.869112	2.422099	-1.567860
C	2.417781	3.077671	0.463211
H	3.093453	2.232044	0.630007
H	3.037453	3.931025	0.146008
H	1.939544	3.320154	1.411805
C	-0.290413	4.492294	0.183038
H	-1.304911	4.828774	-0.048826
H	-0.263498	4.145674	1.218998
H	0.378100	5.359662	0.094345
H	-2.022558	2.406750	0.338375

TS3.44

B3LYP SCF energy:	-2136.27474827 a.u.
B3LYP enthalpy:	-2135.672171 a.u.
B3LYP free energy:	-2135.776932 a.u.
M06 SCF energy in solution:	-2136.74259784 a.u.
M06 enthalpy in solution:	-2136.140021 a.u.
M06 free energy in solution:	-2136.244782 a.u.
Imaginary frequency:	-201.6078 cm-1

Cartesian coordinates

ATOM	X	Y	Z
N	1.190152	-1.700208	0.288075
C	0.883281	-3.110443	0.610847
H	1.424343	-3.781557	-0.061908
C	-0.639320	-3.171916	0.423059
N	-1.001954	-1.748365	0.242847
H	-1.159446	-3.589801	1.289314
C	2.560064	-1.254344	0.210254
C	-2.389357	-1.387878	0.116517
C	-5.128549	-0.824821	-0.104431
C	-3.141172	-1.159284	1.285224
C	-2.989682	-1.382868	-1.157896
C	-4.355323	-1.087962	-1.239742
C	-4.504639	-0.875512	1.146227
C	-2.515010	-1.215948	2.657847
C	-2.207166	-1.695364	-2.410796
H	-4.827288	-1.077787	-2.219907
H	-5.092868	-0.694112	2.043205
C	-6.596440	-0.486379	-0.227006
C	5.245150	-0.455627	0.046090
C	3.243858	-1.376796	-1.017980
C	3.224480	-0.827505	1.378282
C	4.558803	-0.419458	1.262346
C	4.576317	-0.958223	-1.074429
C	2.591128	-1.975798	-2.239964
C	2.562787	-0.841318	2.735229
H	5.076486	-0.077940	2.156034
H	5.106642	-1.036978	-2.020945
C	6.672855	0.027750	-0.056796
H	-2.078852	-2.201252	2.867592
H	-1.716229	-0.473580	2.761620
H	-1.713063	-2.673148	-2.347685

H	-1.426277	-0.950354	-2.600828
H	-6.745239	0.594247	-0.354260
H	-7.153212	-0.787202	0.666768
H	-7.050426	-0.979545	-1.093184
H	2.214961	-1.847523	3.002610
H	1.699441	-0.170263	2.777969
H	3.302674	-2.013003	-3.070250
H	1.728183	-1.385483	-2.560254
H	7.245020	-0.561565	-0.781732
H	7.186308	-0.027403	0.908866
H	6.711233	1.073972	-0.388178
C	0.078968	-0.949896	0.127817
Ru	0.108686	1.108139	-0.194142
Cl	-0.065890	1.500159	2.233963
Cl	0.469225	0.822540	-2.618864
C	-1.467873	2.028804	-0.641328
H	3.274160	-0.528136	3.505458
H	2.251512	-3.003159	-2.053646
H	-2.872990	-1.720351	-3.278876
H	-3.267075	-1.021494	3.428545
H	-0.933837	-3.747138	-0.462233
H	1.189970	-3.334942	1.638495
C	0.132202	3.454668	-0.627830
C	1.376483	2.795639	-0.350736
H	-1.686747	2.067565	-1.713946
H	-0.054031	3.629739	-1.685811
H	2.046748	2.585041	-1.179827
C	-2.612962	2.432430	0.235106
H	-3.101878	3.338137	-0.150837
H	-3.355759	1.624153	0.176664
H	-2.337682	2.563672	1.281141
C	-0.367402	4.510362	0.336484
H	-1.386311	4.837165	0.114093
H	-0.323285	4.149459	1.367360
H	0.285642	5.388831	0.252355
H	1.833997	2.973885	0.620983

3.45

B3LYP SCF energy:	-1286.47272499 a.u.
B3LYP enthalpy:	-1285.949811 a.u.
B3LYP free energy:	-1286.045471 a.u.
M06 SCF energy in solution:	-1286.94855166 a.u.
M06 enthalpy in solution:	-1286.425638 a.u.
M06 free energy in solution:	-1286.521298 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.376970	1.011158	-0.587893
O	0.604373	2.177692	1.228031
O	1.191128	3.189027	-0.650484
N	0.812205	-1.708100	0.232829
N	-1.367956	-1.465660	0.045576
C	-0.183683	-0.801666	-0.050027
C	0.305157	-3.089594	0.253315
C	-1.186613	-2.856486	0.507762

C	2.193015	-1.364752	0.066110
C	3.145506	-1.767015	1.019762
C	4.477177	-1.376230	0.833395
C	4.877523	-0.570385	-0.236493
C	3.902005	-0.150827	-1.144283
C	2.561963	-0.549791	-1.036239
C	2.771368	-2.550019	2.257148
C	6.324125	-0.169154	-0.410836
C	1.521663	-0.066341	-1.991317
C	-2.673148	-0.872889	0.121024
C	-3.591000	-1.133665	-0.915078
C	-4.874627	-0.589114	-0.821177
C	-5.265505	0.195311	0.269174
C	-4.331315	0.428816	1.281699
C	-3.033985	-0.095515	1.237638
C	-3.201673	-1.955976	-2.122104
C	-6.668087	0.750445	0.361134
C	-2.067422	0.196780	2.361438
C	-1.058325	1.416684	-1.629377
C	1.069184	3.206810	0.601783
C	1.465648	4.416456	1.417906
H	0.772480	-3.693474	1.032347
H	0.487258	-3.573003	-0.717049
H	-1.828033	-3.545095	-0.047736
H	-1.441268	-2.932519	1.574226
H	5.215934	-1.684599	1.570512
H	4.181623	0.491469	-1.976476
H	1.806355	-2.222346	2.658922
H	3.525646	-2.411201	3.037671
H	2.704002	-3.630056	2.067108
H	6.830031	-0.810761	-1.144904
H	6.878358	-0.249837	0.530244
H	6.412549	0.862458	-0.768850
H	0.970739	-0.888257	-2.459134
H	1.939370	0.582982	-2.765594
H	-5.583235	-0.775862	-1.625610
H	-4.616726	1.036440	2.138007
H	-2.234519	-1.639301	-2.526704
H	-3.952403	-1.859868	-2.912278
H	-3.117995	-3.024834	-1.883599
H	-7.352526	0.027194	0.824872
H	-7.070782	0.987486	-0.629590
H	-6.699100	1.662279	0.966507
H	-1.345947	0.973983	2.082793
H	-1.486176	-0.688088	2.644468
H	-2.609009	0.539235	3.249040
H	-1.006371	2.359838	-2.193945
H	-1.998863	0.866797	-1.721849
H	0.615458	4.748206	2.023307
H	2.270215	4.143832	2.109855
H	1.798785	5.227212	0.767379

TS3.46

B3LYP SCF energy: -1443.67459973 a.u.

B3LYP enthalpy: -1443.035410 a.u.

B3LYP free energy:	-1443.143404 a.u.
M06 SCF energy in solution:	-1444.08729563 a.u.
M06 enthalpy in solution:	-1443.448106 a.u.
M06 free energy in solution:	-1443.556100 a.u.
Imaginary frequency:	-126.6487 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.421739	0.729941	0.015832
O	1.030305	3.403305	-1.968168
O	1.651058	2.513307	0.020579
N	0.473114	-2.140061	-0.241117
N	-1.654116	-1.632090	-0.375992
C	-0.426565	-1.103040	-0.136966
C	-0.126049	-3.345331	-0.841864
C	-1.619461	-3.090763	-0.607941
C	1.875837	-1.855845	-0.323304
C	2.800245	-2.634662	0.396550
C	4.154202	-2.291741	0.320796
C	4.605096	-1.190429	-0.419260
C	3.662981	-0.423449	-1.105233
C	2.294541	-0.746668	-1.106467
C	2.364774	-3.790498	1.267286
C	6.077022	-0.853153	-0.484116
C	1.287695	0.102240	-1.798280
C	-2.920591	-0.966577	-0.273145
C	-3.484897	-0.395372	-1.430240
C	-4.737370	0.215172	-1.324394
C	-5.436184	0.269451	-0.112569
C	-4.847965	-0.309700	1.015078
C	-3.598179	-0.938467	0.958391
C	-2.742611	-0.398994	-2.745093
C	-6.796915	0.922164	-0.035524
C	-3.008211	-1.563127	2.202266
C	-1.094233	1.787395	-0.088440
C	1.716381	3.387339	-0.943225
H	0.224946	-4.261059	-0.361077
H	0.122889	-3.396975	-1.910782
H	-2.242861	-3.362340	-1.464664
H	-1.996416	-3.626499	0.273216
H	4.874241	-2.886513	0.879639
H	3.984026	0.445312	-1.674327
H	1.422367	-3.570655	1.780864
H	3.123279	-4.009176	2.025282
H	2.215225	-4.712439	0.688547
H	6.234112	0.223346	-0.608166
H	6.562200	-1.353148	-1.333318
H	6.602160	-1.171264	0.423101
H	0.608011	-0.468192	-2.439428
H	1.715603	0.945325	-2.338141
H	-5.174543	0.668131	-2.211819
H	-5.373669	-0.274535	1.967020
H	-1.825477	0.197093	-2.677129
H	-3.363879	0.021265	-3.541380
H	-2.447808	-1.410995	-3.047927
H	-7.569984	0.281425	-0.479862
H	-6.815546	1.873161	-0.579675

H	-7.088881	1.119472	1.000819
H	-1.962289	-1.274195	2.346898
H	-3.035586	-2.659922	2.158761
H	-3.570886	-1.261065	3.090723
H	-2.133251	1.463742	0.019168
C	0.682994	0.604483	2.286841
C	-0.337712	1.560784	2.262031
H	0.377791	-0.419369	2.497365
H	-1.353141	1.194580	2.390159
C	2.763546	4.481385	-0.695625
H	3.740356	4.035146	-0.477003
H	2.842808	5.137154	-1.565678
H	2.481432	5.079024	0.180088
C	-0.112729	3.026984	2.537046
H	0.712875	3.410072	1.932884
H	-1.009229	3.615859	2.322950
H	0.136895	3.168188	3.599168
C	2.123402	0.928824	2.629703
H	2.785254	0.109566	2.330388
H	2.459988	1.837565	2.127680
H	2.231644	1.059268	3.717476
H	-0.949321	2.857954	-0.263755

TS3.49

B3LYP SCF energy:	-1443.68952604 a.u.
B3LYP enthalpy:	-1443.049442 a.u.
B3LYP free energy:	-1443.155367 a.u.
M06 SCF energy in solution:	-1444.09586616 a.u.
M06 enthalpy in solution:	-1443.455782 a.u.
M06 free energy in solution:	-1443.561707 a.u.
Imaginary frequency:	-231.1418 cm-1

Cartesian coordinates

ATOM	X	Y	Z
O	-0.759744	2.648139	-0.879667
O	0.535443	3.190709	0.832189
C	1.146077	0.396829	2.147738
C	-0.173006	3.519454	-0.178825
H	1.114824	-0.637121	2.516458
C	-1.629108	1.244086	1.580581
C	-0.835662	0.977332	2.740458
H	-1.932577	2.274648	1.412645
H	-2.341133	0.500880	1.247346
H	-0.963651	-0.012260	3.176703
C	-0.275161	4.989183	-0.546097
H	0.627624	5.288971	-1.092198
H	-0.334604	5.605252	0.355932
H	-1.142563	5.168378	-1.185721
Ru	0.262632	0.980941	0.566760
C	0.049377	-0.917414	-0.108416
C	1.560280	1.031272	-1.118463
N	1.153930	-1.684464	-0.412535
N	-1.033323	-1.610495	-0.562151
C	2.715505	0.162447	-0.758818
H	1.004962	0.658054	-1.987616

H	1.872856	2.059844	-1.314613
C	0.825709	-2.776406	-1.350481
C	2.495576	-1.182126	-0.375371
C	-0.682783	-2.912419	-1.160324
C	-2.424096	-1.283382	-0.428081
C	4.024234	0.654175	-0.703354
H	1.365357	-3.694717	-1.115210
H	1.089371	-2.473109	-2.373165
C	3.545913	-1.995914	0.071353
H	-1.226242	-3.064167	-2.097281
H	-0.942009	-3.731202	-0.476359
C	-3.038583	-0.470974	-1.400353
C	-3.168954	-1.853111	0.622759
C	5.103705	-0.144862	-0.302375
H	4.199925	1.689797	-0.987240
C	4.844175	-1.460097	0.083262
C	3.324916	-3.401628	0.583020
C	-4.410516	-0.224184	-1.280902
C	-2.256453	0.149005	-2.532506
C	-4.537454	-1.573762	0.698102
C	-2.525208	-2.738296	1.666156
C	6.509667	0.410261	-0.291499
H	5.663925	-2.087896	0.426922
H	2.362952	-3.494443	1.098763
H	4.114685	-3.678873	1.288619
H	3.341953	-4.149704	-0.221909
C	-5.176624	-0.758237	-0.240447
H	-4.892036	0.405373	-2.026282
H	-1.713535	1.036310	-2.186645
H	-2.930252	0.455925	-3.338934
H	-1.520221	-0.546125	-2.950776
H	-5.115843	-2.002453	1.514179
H	-1.519407	-2.394142	1.926629
H	-2.433970	-3.776630	1.319676
H	-3.127200	-2.758050	2.579944
H	6.893880	0.543087	-1.311635
H	7.200100	-0.256210	0.235947
H	6.549413	1.391943	0.195257
C	-6.649609	-0.441903	-0.121606
H	-7.183061	-1.216138	0.439815
H	-7.120382	-0.350735	-1.106573
H	-6.808351	0.510113	0.402135
C	-0.590666	2.102763	3.727197
H	0.160480	1.852124	4.480940
H	-0.276559	3.008308	3.200940
H	-1.528044	2.320499	4.257015
C	2.196238	1.227957	2.830578
H	2.209180	1.099933	3.922231
H	3.167934	0.869792	2.456168
H	2.114765	2.289229	2.583577

***E*-butene**

B3LYP SCF energy:	-157.22387052 a.u.
B3LYP enthalpy:	-157.108916 a.u.
B3LYP free energy:	-157.142690 a.u.

M06 SCF energy in solution: -157.13351694 a.u.
M06 enthalpy in solution: -157.018562 a.u.
M06 free energy in solution: -157.052336 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.538154	-0.395563	0.000045
H	-0.392445	-1.477890	-0.000051
C	0.538151	0.395548	0.000018
H	0.392391	1.477873	-0.000028
C	-1.963802	0.079262	-0.000030
H	-2.508227	-0.289062	-0.880482
H	-2.508226	-0.289044	0.880481
H	-2.022894	1.173244	0.000016
C	1.963808	-0.079246	-0.000013
H	2.022921	-1.173239	-0.000229
H	2.508268	0.289234	-0.880395
H	2.508194	0.288879	0.880568

ethylene

B3LYP SCF energy: -78.58582485 a.u.
B3LYP enthalpy: -78.530604 a.u.
B3LYP free energy: -78.555465 a.u.
M06 SCF energy in solution: -78.53967110 a.u.
M06 enthalpy in solution: -78.484450 a.u.
M06 free energy in solution: -78.509311 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.000000	0.000000	0.665610
H	0.000000	0.923760	1.239622
H	0.000000	-0.923760	1.239622
C	0.000000	0.000000	-0.665610
H	0.000000	-0.923760	-1.239622
H	0.000000	0.923760	-1.239622

propene

B3LYP SCF energy: -117.90521904 a.u.
B3LYP enthalpy: -117.820087 a.u.
B3LYP free energy: -117.850105 a.u.
M06 SCF energy in solution: -117.83720744 a.u.
M06 enthalpy in solution: -117.752075 a.u.
M06 free energy in solution: -117.782093 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.139458	-0.504279	0.000000
H	0.779347	-1.538748	0.000000
H	1.781316	-0.366166	0.880645
H	1.781316	-0.366166	-0.880645
C	0.000000	0.475026	0.000000
H	0.277926	1.530165	0.000000
C	-1.293406	0.149794	0.000000

H	-1.621773	-0.887951	0.000000
H	-2.074446	0.905621	0.000000

_Z_-butene

B3LYP SCF energy:	-157.22172615 a.u.
B3LYP enthalpy:	-157.106612 a.u.
B3LYP free energy:	-157.140805 a.u.
M06 SCF energy in solution:	-157.13186478 a.u.
M06 enthalpy in solution:	-157.016751 a.u.
M06 free energy in solution:	-157.050944 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.669341	0.664333	0.000017
H	-1.169678	1.633564	-0.000021
C	0.669331	0.664372	0.000011
H	1.169571	1.633649	-0.000063
C	-1.593233	-0.521956	-0.000003
H	-2.250579	-0.505579	-0.880214
H	-1.060367	-1.476899	0.000055
H	-2.250674	-0.505532	0.880113
C	1.593246	-0.521949	0.000000
H	1.060349	-1.476859	0.000189
H	2.250550	-0.505677	-0.880247
H	2.250810	-0.505469	0.880041

3.8-mono

B3LYP SCF energy:	-1536.03380584 a.u.
B3LYP enthalpy:	-1535.369804 a.u.
B3LYP free energy:	-1535.467919 a.u.
M06 SCF energy in solution:	-1536.45382313 a.u.
M06 enthalpy in solution:	-1535.789821 a.u.
M06 free energy in solution:	-1535.887936 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.433569	0.803673	0.203201
O	-1.497047	2.507263	-1.643022
O	-1.465675	2.692377	0.535121
N	-0.646777	-2.053470	-0.180673
N	1.506822	-1.764092	0.066336
C	0.308479	-1.103782	-0.019586
C	-0.163013	-3.422013	0.008730
H	-0.568969	-4.102708	-0.744695
H	-0.445125	-3.800904	1.000899
C	1.351539	-3.225791	-0.120687
H	1.923546	-3.776159	0.631339
H	1.722979	-3.518301	-1.111366
C	-2.050880	-1.648581	-0.108192
C	-2.574496	-1.713603	1.351999
H	-1.915671	-1.121824	1.999966
H	-2.542608	-2.752136	1.712201
C	-4.016354	-1.174427	1.418790

H	-4.373490	-1.227230	2.455743
C	-4.920351	-2.036282	0.513572
H	-4.933716	-3.076276	0.870299
H	-5.954985	-1.670763	0.556240
C	-4.402625	-1.976871	-0.938705
H	-5.043817	-2.590335	-1.585335
C	-2.960625	-2.530014	-0.995837
H	-2.584819	-2.522969	-2.027621
H	-2.950080	-3.573736	-0.647823
C	-4.419458	-0.512705	-1.422354
H	-4.082135	-0.449146	-2.465400
H	-5.446820	-0.123432	-1.394494
C	-3.505821	0.357954	-0.517161
H	-3.536751	1.385593	-0.882417
C	-2.077931	-0.200333	-0.632990
H	-1.767710	-0.197599	-1.688789
C	-4.026177	0.289245	0.933084
H	-3.404476	0.916858	1.583082
H	-5.046680	0.692904	0.980711
C	2.830355	-1.233943	-0.106652
C	3.708105	-1.204960	0.992712
C	5.015673	-0.745515	0.791287
H	5.693922	-0.710991	1.641364
C	5.473371	-0.339619	-0.464414
C	4.587683	-0.417479	-1.545347
H	4.930025	-0.123816	-2.535445
C	3.271883	-0.864060	-1.395511
C	3.285620	-1.687245	2.361305
H	3.952337	-1.293821	3.134654
H	3.325421	-2.783277	2.427731
H	2.262337	-1.388988	2.602831
C	6.878796	0.182473	-0.651612
H	6.902837	1.279097	-0.601244
H	7.286251	-0.104933	-1.626946
H	7.553800	-0.194500	0.123620
C	2.354332	-0.925786	-2.595827
H	1.902661	-1.916841	-2.719784
H	2.905523	-0.695333	-3.512107
H	1.528714	-0.210199	-2.510442
C	0.262675	0.942326	2.056745
C	1.309731	1.782392	-0.239509
C	1.408132	1.800359	1.342879
H	0.658615	0.082452	2.599841
H	-0.375417	1.566099	2.691062
H	2.330967	1.251645	1.554219
H	2.059090	1.112102	-0.650044
C	1.456426	3.208879	1.948928
H	1.635603	3.140578	3.027809
H	2.261415	3.808173	1.509443
H	0.508068	3.730794	1.793796
C	1.331789	3.101580	-0.984250
H	2.353711	3.512152	-0.965882
H	1.058503	2.948837	-2.032061
H	0.663615	3.856140	-0.568055
N	-1.811077	3.177678	-0.626137
O	-2.413973	4.243757	-0.676197

3.9-mono

B3LYP SCF energy:	-1536.03471628 a.u.
B3LYP enthalpy:	-1535.370905 a.u.
B3LYP free energy:	-1535.468727 a.u.
M06 SCF energy in solution:	-1536.45385846 a.u.
M06 enthalpy in solution:	-1535.790047 a.u.
M06 free energy in solution:	-1535.887869 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.332880	0.865344	-0.173476
O	-1.772311	2.154169	1.761104
O	-1.245855	2.867225	-0.237983
N	-0.695674	-2.016420	-0.204171
N	1.467367	-1.778888	-0.013413
C	0.292275	-1.086998	-0.105072
C	-0.239922	-3.394924	-0.004610
H	-0.659347	-4.069237	-0.756601
H	-0.534866	-3.763594	0.987014
C	1.280924	-3.239898	-0.133013
H	1.835432	-3.765172	0.650150
H	1.651734	-3.589862	-1.105200
C	-2.095007	-1.602464	-0.115375
C	-2.646338	-1.792583	1.323122
H	-2.008878	-1.243787	2.027453
H	-2.607154	-2.856484	1.597188
C	-4.098526	-1.279358	1.405904
H	-4.474930	-1.438682	2.424788
C	-4.978540	-2.048633	0.400616
H	-4.992225	-3.121285	0.642146
H	-6.015853	-1.693753	0.463658
C	-4.432997	-1.832939	-1.026084
H	-5.060505	-2.370988	-1.748851
C	-2.993395	-2.387119	-1.104061
H	-2.589852	-2.285463	-2.120444
H	-2.996813	-3.459392	-0.858680
C	-4.436306	-0.324841	-1.357258
H	-4.077840	-0.160817	-2.382971
H	-5.462443	0.065029	-1.311803
C	-3.541026	0.443465	-0.343251
H	-3.545353	1.508989	-0.593043
C	-2.120924	-0.118036	-0.492790
H	-1.821129	-0.019864	-1.565840
C	-4.113565	0.223512	1.073043
H	-3.530391	0.789249	1.803167
H	-5.143700	0.603813	1.110042
C	2.802177	-1.274525	0.123028
C	3.315229	-1.063007	1.421302
C	4.625329	-0.598488	1.552902
H	5.020276	-0.419420	2.550761
C	5.445707	-0.368954	0.440653
C	4.929407	-0.648575	-0.825624
H	5.560713	-0.506430	-1.700642
C	3.620544	-1.115090	-1.009789
C	2.494224	-1.378463	2.651741

H	2.986539	-0.999980	3.552402
H	2.373903	-2.463221	2.776456
H	1.489746	-0.948781	2.605462
C	6.847189	0.168933	0.612193
H	6.836227	1.254291	0.777246
H	7.461195	-0.021784	-0.273795
H	7.346876	-0.283155	1.476208
C	3.159174	-1.479492	-2.403788
H	3.559494	-2.459068	-2.698593
H	3.520866	-0.753551	-3.139775
H	2.071131	-1.528095	-2.483056
C	0.985475	1.393025	-1.590352
C	1.741296	2.045438	-0.323586
C	1.072955	1.645705	1.041835
H	1.602351	0.596459	-2.004773
H	2.716841	1.551261	-0.324997
H	1.688834	0.989741	1.650703
H	0.703104	2.499320	1.610234
C	0.490406	2.315667	-2.693136
H	1.328806	2.822488	-3.194315
H	-0.026601	1.724298	-3.459457
H	-0.200904	3.078468	-2.328137
O	-2.427249	4.133228	1.094943
N	-1.840328	3.074304	0.905863
C	1.901552	3.568194	-0.426720
H	2.506708	3.933932	0.410508
H	2.405375	3.856157	-1.356174
H	0.929215	4.065967	-0.388948

3.15-mono

B3LYP SCF energy:	-1496.72425741 a.u.
B3LYP enthalpy:	-1496.090256 a.u.
B3LYP free energy:	-1496.185918 a.u.
M06 SCF energy in solution:	-1497.16342619 a.u.
M06 enthalpy in solution:	-1496.529425 a.u.
M06 free energy in solution:	-1496.625087 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.308622	0.947510	-0.204367
O	-1.784914	2.234515	1.690059
O	-1.258102	2.926264	-0.316010
N	-0.582577	-1.943942	-0.150158
N	1.572447	-1.629960	0.027371
C	0.374828	-0.981331	-0.083633
C	-0.081503	-3.299102	0.095489
H	-0.481514	-4.013086	-0.629967
H	-0.360362	-3.641407	1.101127
C	1.433344	-3.099351	-0.045582
H	2.007551	-3.582011	0.750629
H	1.811191	-3.467430	-1.008376
C	-1.994713	-1.569994	-0.078993
C	-2.545960	-1.728840	1.362876
H	-1.928664	-1.137438	2.050528
H	-2.475859	-2.781364	1.672519

C	-4.013673	-1.257296	1.423136
H	-4.390016	-1.394416	2.445260
C	-4.865294	-2.085497	0.440367
H	-4.847523	-3.149638	0.716826
H	-5.913231	-1.760733	0.487958
C	-4.319897	-1.900226	-0.990548
H	-4.927800	-2.480022	-1.697619
C	-2.864170	-2.414083	-1.044206
H	-2.458660	-2.334614	-2.061789
H	-2.837070	-3.477196	-0.762895
C	-4.366517	-0.404374	-1.371172
H	-4.007966	-0.263265	-2.400241
H	-5.404378	-0.045067	-1.342747
C	-3.500132	0.423775	-0.379648
H	-3.535761	1.480128	-0.664278
C	-2.062952	-0.099549	-0.506349
H	-1.763994	-0.030511	-1.581040
C	-4.072310	0.232769	1.040829
H	-3.509955	0.839362	1.754186
H	-5.113604	0.582834	1.061876
C	2.888868	-1.072287	0.132388
C	3.408317	-0.802685	1.417517
C	4.698991	-0.280181	1.518951
H	5.097633	-0.055965	2.506177
C	5.495446	-0.047783	0.389808
C	4.976115	-0.384671	-0.861120
H	5.590475	-0.241437	-1.747944
C	3.686248	-0.911678	-1.014881
C	2.615826	-1.116119	2.667131
H	3.094972	-0.679758	3.548510
H	2.554783	-2.200503	2.832071
H	1.589545	-0.742142	2.615899
C	6.875317	0.551929	0.528454
H	6.820054	1.634016	0.705230
H	7.472612	0.396666	-0.375586
H	7.418698	0.115246	1.373989
C	3.225929	-1.338690	-2.391450
H	3.666663	-2.308178	-2.660757
H	3.546925	-0.620715	-3.153649
H	2.140327	-1.438404	-2.455993
C	0.995004	1.475983	-1.631171
C	1.679855	2.197591	-0.378620
C	1.071101	1.802455	1.002324
H	1.646543	0.695174	-2.020436
H	1.574772	3.275229	-0.520901
H	2.730771	1.896299	-0.388126
H	1.718567	1.175989	1.608493
H	0.668015	2.642986	1.564782
C	0.523983	2.409399	-2.733750
H	1.379177	2.940553	-3.180505
H	0.040437	1.841636	-3.538523
H	-0.184026	3.155192	-2.362701
O	-2.489490	4.181484	0.981460
N	-1.870183	3.137397	0.816677

3.16-mono

B3LYP SCF energy:	-1496.72303339 a.u.
B3LYP enthalpy:	-1496.088920 a.u.
B3LYP free energy:	-1496.185017 a.u.
M06 SCF energy in solution:	-1497.16320049 a.u.
M06 enthalpy in solution:	-1496.529087 a.u.
M06 free energy in solution:	-1496.625184 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.408766	0.856085	0.343563
O	-1.457067	2.679957	-1.373330
O	-1.485940	2.687787	0.812274
N	-0.554284	-1.965370	-0.239997
N	1.590400	-1.645855	0.056078
C	0.378091	-1.009482	-0.007598
C	-0.042938	-3.332869	-0.133689
H	-0.421605	-3.970664	-0.937240
H	-0.332471	-3.783001	0.826044
C	1.469759	-3.096388	-0.224613
H	2.041428	-3.681327	0.501103
H	1.862985	-3.317987	-1.225287
C	-1.968629	-1.590546	-0.188707
C	-2.544453	-1.761185	1.242728
H	-1.924152	-1.201236	1.953796
H	-2.503286	-2.820582	1.534802
C	-3.999826	-1.254643	1.288067
H	-4.393757	-1.382518	2.304948
C	-4.850771	-2.072078	0.294733
H	-4.855222	-3.133443	0.581822
H	-5.893871	-1.729795	0.321561
C	-4.280835	-1.906228	-1.129308
H	-4.884295	-2.487038	-1.839293
C	-2.826802	-2.428167	-1.165892
H	-2.412133	-2.347701	-2.179458
H	-2.807992	-3.491916	-0.885287
C	-4.309019	-0.413932	-1.516653
H	-3.932779	-0.276659	-2.539185
H	-5.344383	-0.045723	-1.505237
C	-3.449040	0.412354	-0.521760
H	-3.488127	1.460920	-0.820936
C	-2.006129	-0.109922	-0.618421
H	-1.659724	-0.033207	-1.660115
C	-4.023744	0.237418	0.898724
H	-3.444369	0.833074	1.614210
H	-5.054714	0.615159	0.930623
C	2.895632	-1.066956	-0.099250
C	3.789484	-1.083703	0.986761
C	5.078687	-0.569423	0.798374
H	5.769575	-0.570568	1.638866
C	5.502570	-0.064353	-0.432914
C	4.601248	-0.095593	-1.503406
H	4.917264	0.276717	-2.475716
C	3.303113	-0.593882	-1.365620
C	3.402907	-1.667137	2.326274
H	4.088020	-1.328431	3.109354
H	3.445995	-2.764855	2.311857

H	2.385174	-1.391392	2.615093
C	6.888191	0.512495	-0.606653
H	6.870537	1.608617	-0.545492
H	7.310926	0.251071	-1.583032
H	7.573080	0.152329	0.167685
C	2.366550	-0.599063	-2.552560
H	1.931650	-1.589254	-2.731272
H	2.897018	-0.300024	-3.461235
H	1.528911	0.092869	-2.407896
C	0.242464	0.842746	2.223526
C	1.311833	1.915811	0.026418
C	1.350353	1.790064	1.593474
H	0.658965	-0.054743	2.682998
H	-0.422991	1.382595	2.902961
H	2.323296	1.363720	1.851548
H	2.094520	1.320915	-0.436080
C	1.310720	3.329717	-0.517934
H	2.322506	3.753615	-0.418116
H	1.047793	3.345078	-1.579093
H	0.620454	3.985727	0.017577
N	-1.819864	3.254880	-0.313871
O	-2.458366	4.300639	-0.295497
H	1.232207	2.788945	2.018660